SUPPORTING INFORMATION

Stereocontrolled Spirocyclization of *exo*-Glycals with Arylamines for the Synthesis of (1*S*)-Spiro- Tetrahydroquinoline Glycosides

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Contents

Experimental Section

General Information of reagents and instrumentation:

All purchased chemicals were of reagent grade. All reactions were carried out under a nitrogen atmosphere and monitored by TLC analysis (layer thickness: 250 μm). Column chromatography was carried out with silica gel 60 (70–230 mesh for gravity column, or 230–400 mesh for flash column). Commercially available reagents were directly used without purification unless otherwise noted. Dichloromethane, 1,2-dichloroethane, ethyl acetate, and hexanes were purchased. Proton were NMR spectra recorded at a Bruker spectrometer (400 or 500 MHz) with $CDCl_3$ (δ_H 7.24) and Water-d_2 (δ_H 4.65) as the internal standard; Carbon-13 NMR spectra were recorded at 100 or 125 MHz with $CDCl_3$ [δ_C 77.0 (central line of a triplet)] and Water-d_2. Splitting patterns were shown by abbreviations, such as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). High-resolution mass spectra (HRMS) were a Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometer or an electron ionization time-of-flight (EI-TOF) mass spectrometer.

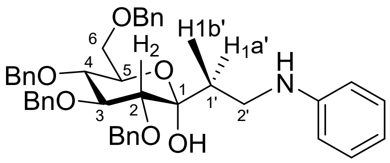
Experimental Procedures and Spectroscopic Characterization Data.

Typical Procedure for Synthesis of *C,O*-glycosides 3a-3r.

To a solution of *exo*-glycals **1** (0.09 mmol), arylamines (0.11 mmol) and acetic acid (0.68 mmol) in dichloroethane (DCE) (2.0 mL) was added $ZnCl_2$ (0.14 mmol). The reaction mixture was stirred at 55 °C under N_2 for 8 h. After the reaction was complete, CH_2Cl_2 (50 mL) was added to the reaction mixture, washed twice with H_2O (20 mL for each), twice with brine (20 mL for each), and dried over $MgSO_4$. The collected organic layer was concentrated under reduced pressure. Finally, the reaction mixture was purified by silica gel column chromatography with *n*-hexane/ethyl acetate (3/1) to give *C,O*-glycosides **3a-3r** in 71–85% yields.

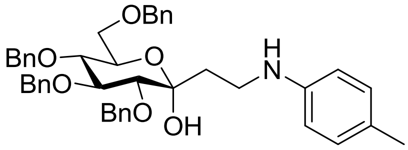
Spectroscopic Characterization Data of 3a-3r.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-1-(2-(phenylamino)ethyl)tetrahydro-2H-pyran-1-ol (3a)[S1]



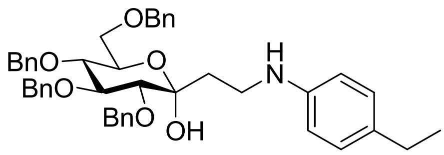
Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the pale yellow oil **3a** (50.4 mg, 85%): $[\alpha]^{25}_{D}$ +8.3 (*c* 0.32, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.11 (23H, m, ArH), 6.76 (1H, dd, *J* = 7.2 Hz, *J* = 7.2 Hz, ArH), 6.63 (1H, m, ArH), 4.95 (1H, d, *J* = 11.2 Hz, CH_2Ph), 4.91 (2H, d, *J* = 12.0 Hz, CH_2Ph), 4.88 (1H, d, *J* = 12.0 Hz, CH_2Ph), 4.83 (1H, d, *J* = 10.8 Hz, CH_2Ph), 4.68 (1H, d, *J* = 11.2 Hz, CH_2Ph), 4.62 (1H, d, *J* = 12.0 Hz, CH_2Ph), 4.57 (1H, d, *J* = 10.0 Hz, CH_2Ph), 4.54 (1H, d, *J* = 12.0 Hz, CH_2Ph), 4.07-4.02 (2H, m, H3, H5), 3.75 (1H, dd, *J* = 4.0 Hz, *J* = 10.8 Hz, H6a), 3.70-3.65 (2H, m, H4, H6b), 3.49-3.43 (1H, m, H2a'), 3.37 (1H, d, *J* = 9.2 Hz, H2), 3.16-3.11 (1H, m, H2b'), 2.13-2.04 (1H, m, H1a'), 1.71-1.65 (1H, m, H1b'). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.8, 138.5, 138.2, 138.1, 137.8, 129.1, 129.1, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128,3, 127.9, 127.8, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.6, 118.8, 114.4, 114.4, 98.7 (C-1), 83.5 (C-3), 82.2 (C-5), 78.4 (C-4), 75,6 ($PhCH_2$ at C-3), 75.4 ($PhCH_2$ at C-4), 74.8 ($PhCH_2$ at C-6), 73.3 ($PhCH_2$ at C-2), 71.0 (C-2), 68.8 (C-6), 39.6 (C-2'), 35.4 (C-1'); HRMS (EI): *m*/*z* calcd for $C_{42}H_{45}NO_6$ (M^+) 659.3247, found 659.3238.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-1-(2-(p-tolylamino)ethyl)tetrahydro-2H-pyran-1-ol (3b)



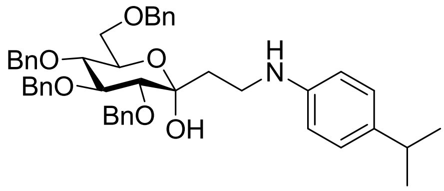
Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the pale yellow oil **3b** (50.8 mg, 84%): $[\alpha]^{25}_{D}$ +10.7 (c 0.51, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.17 (m, 20H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 4.95 (d, *J* = 11.2 Hz, 1H), 4.90 (brs, 2H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.07-4.01 (m, 2H), 3.75 (dd, *J* = 4.0 Hz, *J* = 10.8 Hz, 1H), 3.72-3.64 (m, 2H), 3.53-3.46 (m, 1H), 3.35 (d, $J_{2,3}$ = 9.2 Hz, 1H), 3.14-3.09 (m, 1H), 2.23 (s, 3H), 2.13-2.06 (m, 1H), 1.66-1.60 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.4, 138.6, 138.3, 138.1, 137.9, 129.6, 129.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.3, 128,3, 128,3, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.5, 127.5, 115.0, 115.0, 98.8, 83.5, 82.4, 78.5, 75.5, 75.4, 74.8, 73.3, 70.9, 68.9, 40.3, 35.3, 20.4; HRMS (EI): *m/z* calcd for $C_{43}H_{47}NO_6$ (M^+) 673.3403, found 673.3396.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-1-(2-((4-ethylphenyl)amino)ethyl)tetrahydro-2H-pyran-1-ol (3c)



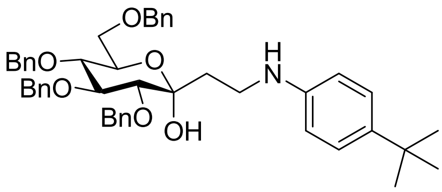
Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the pale yellow oil **3c** (50.1 mg, 81%): $[\alpha]^{25}_{D}$ +9.4 (c 0.72, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.17 (m, 20H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 4.95 (d, *J* = 11.2 Hz, 1H), 4.90 (brs, 2H), 4.83 (d, *J* = 11.2 Hz, 1H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.61 (d, *J* = 12.4 Hz, 1H), 4.57 (d, *J* = 11.2 Hz, 1H), 4.54 (d, *J* = 12.4 Hz, 1H), 4.07-4.01 (m, 2H), 3.75 (dd, *J* = 4.0 Hz, *J* = 10.8 Hz, 1H), 3.69-3.64 (m, 2H), 3.54-3.47 (m, 1H), 3.35 (d, $J_{2,3}$ = 9.2 Hz, 1H), 3.15-3.10 (m, 1H), 2.53 (q, *J* = 7.2 Hz, 2H), 2.14-2.06 (m, 1H), 166-1.60 (m, 1H), 1.18 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.5, 138.6, 138.2, 138.1, 137.9, 135.2, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 115.0, 115.0, 98.8, 83.4, 82.4, 78.5, 75,5, 75.4, 74.8, 73.3, 70.9, 68.9, 40.2, 35.2, 27.9, 15.9. HRMS (EI) *m*/*z* calcd for $C_{44}H_{49}NO_6$ (M^+) 687.3560, found 687.3567.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-1-(2-((4-isopropylphenyl)amino)ethyl)tetrahydro-2H-pyran-1-ol (3d)



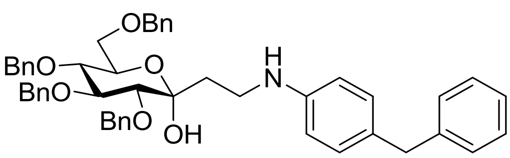
Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the pale yellow oil **3d** (51.6 mg, 82%): $[\alpha]^{25}_{D}$ +12.3 (c 0.81, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.24 (m, 18H), 7.19-7.17 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 2H), 4.95 (d, *J* = 11.2 Hz, 1H), 4.90 (brs, 2H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.62 (d, *J* = 12.4 Hz, 1H), 4.57 (d, *J* = 10.8 Hz, 1H), 4.54 (d, *J* = 12.4 Hz, 1H), 4.08-4.01 (m, 2H), 3.76 (dd, *J* = 4.0 Hz, *J* = 10.8 Hz, 1H), 3.69-3.65 (m, 2H), 3.55-3.48 (m, 1H), 3.34 (d, $J_{2,3}$ = 9.2 Hz, 1H), 3.15-3.10 (m, 1H), 2.83-2.76 (m, 1H), 2.14-2.07 (m, 1H), 166-1.60 (m, 1H), 1.19 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.6, 139.8, 138.6, 138.3, 138.1, 137.9, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7, 127.7, 127.6, 127.5, 127.5, 127.0, 127.0, 114.9, 114.9, 98.8, 83.4, 82.5, 78.6, 75.5, 75.4, 74.8, 73.3, 70.8, 68.9, 40.2, 35.2, 33.2, 24.1, 24.1; HRMS (EI): *m*/*z* calcd for $C_{45}H_{51}NO_6$ (M^+) 701.3716, found 701.3717.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-1-(2-((4-(tert-butyl)phenyl)amino)ethyl)tetrahydro-2H-pyran-1-ol (3e)



Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the pale yellow oil **3e** (52.1 mg, 81%): $[\alpha]^{25}_{D}$ +12.8 (c 0.63, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.24 (m, 18H), 7.19-7.15 (m, 4H), 6.62-6.61 (m, 2H), 4.95 (d, *J* = 11.2 Hz, 1H), 4.90 (brs, 2H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.68 (d, *J* = 11.2 Hz, 1H), 4.62 (d, *J* = 12.4 Hz, 1H), 4.57 (d, *J* = 10.8 Hz, 1H), 4.54 (d, *J* = 12.4 Hz, 1H), 4.08-4.02 (m, 2H), 3.76 (dd, *J* = 4.0 Hz, *J* = 10.8 Hz, 1H), 3.72-3.65 (m, 2H), 3.55-3.49 (m, 1H), 3.35 (d, *J* = 9.2 Hz, 1H), 3.15-3.10 (m, 1H), 2.14-2.07 (m, 1H), 165-1.62 (m, 1H), 1.26 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.2, 142.0, 138.6, 138.2, 138.2, 137.9, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7, 127.6, 127.5, 127.5, 125.9, 125.9, 114.6, 114.6, 98.8, 83.4, 82.5, 78.6, 75.5, 75.4, 74.8, 73.3, 70.8, 68.9, 40.1, 35.2, 33.9, 31.4, 31.4, 31.4; HRMS (EI): *m*/*z* calcd for $C_{46}H_{53}NO_6$ (M^+) 715.3873, found 715.3865.

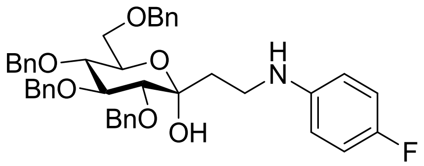
(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-1-(2-((4-benzylphenyl)amino)ethyl)tetrahydro-2H-pyran-1-ol (3f)



Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the pale yellow oil **3f** (56.0 mg, 83%): $[\alpha]^{25}_{D}$ +17.6 (c 0.26, $CHCl_3$); ^1H NMR

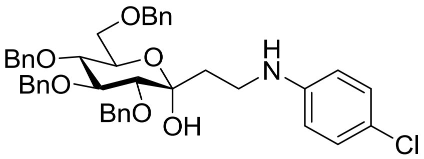
(CDCl$_3$, 400 MHz) δ 7.34-7.15 (, m, 25H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 4.94 (d, *J* = 11.2 Hz, 1H), 4.90 (brs, 2H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 10.8 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.06-4.01 (m, 2H), 3.86 (s, 2H), 3.75 (, dd, *J* = 4.0 Hz, *J* = 10.8 Hz, 1H), 3.69-3.64 (m, 2H), 3.50-3.44 (m, 1H), 3.35 (d, $J_{2,3}$ = 9.4 Hz, 1H), 3.14-3.09 (m, 1H), 2.12-2.05 (m, 1H), 1.66-1.61 (m, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 146.0, 141.8, 138.6, 138.3, 138.1, 137.9, 131.7, 129.6, 129.6, 128.7, 128.7, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 127.9, 127.7, 127.7, 127.7, 127.7, 127.7, 127.7, 127.7, 127.6, 127.6, 127.6, 125.8, 114.8, 114.8, 98.8, 83.5, 82.3, 78.5, 75.6, 75.4, 74.8, 73.3, 70.9, 68.9, 41.0, 41.0, 35.4; HRMS (EI): *m/z* calcd for $C_{49}H_{51}NO_6$ (M$^+$) 749.3716, found 749.3724.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-1-(2-((4-fluorophenyl)amino)ethyl)tetrahydro-2H-pyran-1-ol (3g)



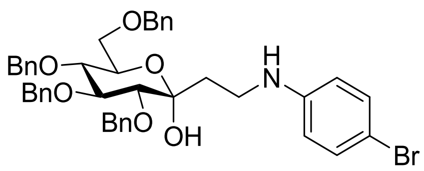
Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the pale yellow oil **3g** (49.4 mg, 81%): $[\alpha]^{25}_D$ +16.2 (c 0.51, CHCl$_3$); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.35-7.25 (m, 18H), 7.20-7.18 (m, 2H), 6.81 (d, *J* = 8.8 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 6.56-6.53 (m, 2H), 4.95 (d, *J* = 11.2 Hz, 1H), 4.91 (d, *J* = 11.2 Hz, 1H), 4.88 (d, *J* = 11.2 Hz, 1H), 4.84 (d, *J* = 10.8 Hz, 1H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 10.8 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.06-4.02 (m, 2H), 3.74 (dd, *J* = 4.0 Hz, *J* = 10.8 Hz, 1H), 3.69-3.64 (m, 2H), 3.42-3.35 (m, 2H), 3.12-3.06 (m, 1H), 2.11-2.03 (m, 1H), 1.69-1.63 (m, 1H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 156.6 (d, *J* = 234.9 Hz), 144.0, 138.5, 138.2, 138.0, 137.8, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7, 127.7, 127.6, 127.6, 127.6, 115.6 (d, *J* = 6.5 Hz), 115.4 (d, *J* = 8.2 Hz), 98.7, 83.5, 82.1, 78.5, 75.63, 75.4, 74.8, 73.3, 70.9, 68.9, 40.5, 35.4; HRMS (EI): *m*/*z* calcd for $C_{42}H_{44}FNO_6$ (M^+) 677.3153, found 677.3143.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-1-(2-((4-chlorophenyl)amino)ethyl)tetrahydro-2H-pyran-1-ol (3h)



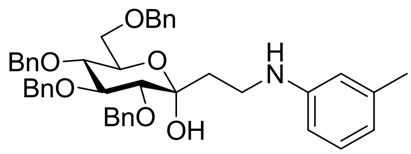
Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the pale yellow oil **3h** (53.1 mg, 85%): $[\alpha]^{25}_{D}$ +9.3 (c 0.43, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.25 (m, 18H), 7.20-7.17 (m, 2H), 7.04-7.02 (m, 2H), 6.48-6.46 (m, 2H), 4.94 (d, *J* = 11.2 Hz, 1H), 4.92 (d, *J* = 9.6 Hz, 1H), 4.87 (d, *J* = 10.8 Hz, 1H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.66 (d, *J* = 11.2 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 10.8 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.09 (brs, 1H), 4.04-4.00 (m, 2H), 3.74 (dd, *J* = 4.0 Hz, *J* = 10.8 Hz, 1H), 3.69-3.63 (m, 2H), 3.38 (d, *J* = 9.2 Hz, 1H), 3.33-3.26 (m, 1H), 3.11-3.06 (m, 1H), 2.08-2.00 (m, 1H), 1.74-1.68 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.6, 138.4, 138.1, 138.0, 137.7, 128.9, 128.9, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.0, 127.8, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7, 127.6, 122.9, 115.1, 115.1, 98.7, 83.5, 81.8, 78.4, 75.6, 75.4, 74.9, 73.4, 71.1, 68.8, 39.5, 35.7; HRMS (EI): *m*/*z* calcd for $C_{42}H_{44}ClNO_6$ (M^+) 693.2857, found 693.2850.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-1-(2-((4-bromophenyl)amino)ethyl)tetrahydro-2H-pyran-1-ol (3i)



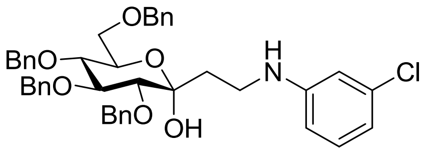
Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the pale yellow oil **3i** (55.0 mg, 83%): $[\alpha]^{25}_{D}$ +11.2 (c 0.32, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.26 (m, 18H), 7.20-7.14 (m, 4H), 6.42 (d, *J* = 8.8 Hz, 2H), 4.94 (d, *J* = 11.2 Hz, 1H), 4.92 (d, *J* = 10.8 Hz, 1H), 4.87 (d, *J* = 10.8 Hz, 1H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.66 (d, *J* = 11.2 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 10.8 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.04-3.99 (m, 2H), 3.74 (dd, *J* = 4.0 Hz, *J* = 10.8 Hz, 1H), 3.69-3.63 (m, 2H), 3.38 (d, *J* = 9.6 Hz, 1H), 3.31-3.24 (m, 1H), 3.11-3.05 (m, 1H), 2.07-2.01 (m, 1H), 1.75-1.69 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.0, 138.4, 138.1, 137.9, 137.7, 131.8, 131.8, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.3, 128.0, 127.8, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 115.5, 115.5, 109.9, 98.6, 83.5, 81.7, 78.3, 75.6, 75.4, 74.9, 73.4, 71.1, 68.8, 39.4, 35.7; HRMS (EI): *m/z* calcd for $C_{42}H_{44}BrNO_6$ (M^+) 737.2352, found 737.2361.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-1-(2-(m-tolylamino)ethyl)tetrahydro-2H-pyran-1-ol (3j)



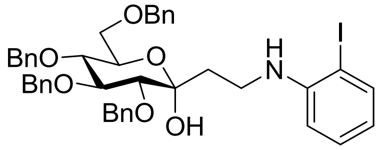
Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the pale yellow oil **3j** (44.8 mg, 74%): $[\alpha]^{25}_{D}$ +16.4 (c 0.33, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.16 (m, 20H), 7.02 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 6.47-6.45 (m, 2H), 4.95 (d, *J* = 11.2 Hz, 1H), 4.91 (d, *J* = 11.2 Hz, 1H), 4.88 (d, J = 11.2 Hz, 1H), 4.83 (d, J = 10.8 Hz, 1H), 4.68 (d, J = 11.2 Hz, 1H), 4.62 (d, J = 12.4 Hz, 1H), 4.57 (d, J = 10.8 Hz, 1H), 4.54 (d, J = 12.4 Hz, 1H), 4.07-4.00 (m, 2H), 3.76 (dd, J = 4.0 Hz, J = 10.8 Hz, 1H), 3.70-3.65 (m, 2H), 3.50-3.43 (m, 1H), 3.36 (d, J = 9.6 Hz, 1H), 3.16-3.10 (m, 1H), 2.24 (s, 3H), 2.13-2.06 (m, 1H), 1.70-1.64 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.8, 138.9, 138.6, 138.2, 138.1, 137.9, 129.0, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.6, 119.9, 115.2, 111.7, 98.7, 83.5, 82.3, 78.5, 75.6, 75.4, 74.8, 73.3, 71.0, 68.8, 39.8, 35.5, 21.5; HRMS (EI): m/z calcd for $C_{43}H_{47}NO_6$ (M^+) 673.3403, found 673.3408.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-1-(2-((3-chlorophenyl)amino)ethyl)tetrahydro-2H-pyran-1-ol (3k)



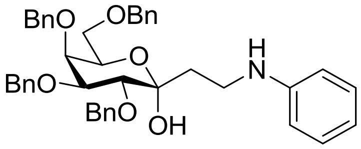
Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the pale yellow oil **3k** (47.4 mg, 76%): $[\alpha]^{25}_D$ +6.3 (c 0.16, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.25 (m, 18H), 7.18-7.16 (m, 2H), 6.98 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H), 6.67 (d, J = 7.6 Hz, 1H), 6.55 (brs, 1H), 6.39 (d, J = 8.0 Hz, 1H), 4.93 (d, J = 10.8 Hz, 1H), 4.89 (d, J = 10.8 Hz, 1H), 4.86 (d, J = 10.8 Hz, 1H), 4.81 (d, J = 10.8 Hz, 1H), 4.69-4.66 (m, 2H), 4.61 (d, J = 12.0 Hz, 1H), 4.56 (d, J = 10.8 Hz, 1H), 4.54 (d, J = 12.0 Hz, 1H), 4.26 (brs, 1H), 4.03-3.98 (m, 2H), 3.75-3.63 (m, 3H), 3.39 (d, J = 9.2 Hz, 1H), 3.26-3.21 (m, 1H), 3.10-3.07 (m, 1H), 2.06-1.99 (m, 1H), 1.76-1.71 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.3, 138.5, 138.1, 138.0, 137.7, 134.9, 130.0, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.0, 127.8, 127.8, 127.8, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7, 127.6, 126.9, 117.8, 113.2, 112.2, 98.6, 83.6, 81.5, 78.3, 75.6, 75.4, 74.9, 73.4, 71.2, 68.7, 39.1, 35.9; HRMS (EI): *m*/*z* calcd for $C_{42}H_{44}ClNO_6$ (M^+) 693.2857, found 693.2851.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-1-(2-((2-iodophenyl)amino)ethyl)tetrahydro-2H-pyran-1-ol (3l)



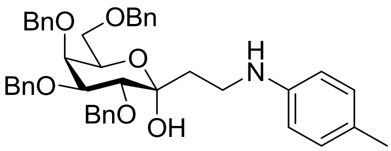
Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the pale yellow oil **3l** (52.9 mg, 75%): $[\alpha]^{25}_{D}$ -0.8 (c 0.38, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.65 (dd, *J* = 1.4 Hz, *J* = 7.6 Hz, 1H), 7.33-7.25 (m, 18H), 7.20-7.17 (m, 2H), 7.16 (dd, *J* = 1.4 Hz, *J* = 8.0 Hz, 1H), 6.60 (dd, *J* = 1.4 Hz, *J* = 8.0 Hz, 1H), 6.47 (dd, *J* = 1.4 Hz, *J* = 7.6 Hz, 1H), 4.95 (d, *J* = 11.2 Hz, 1H), 4.90 (d, *J* = 11.2 Hz, 1H), 4.87 (d, *J* = 10.8 Hz, 1H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.68 (d, *J* = 11.2 Hz, 1H), 4.60 (d, *J* = 11.2 Hz, 2H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.25 (brs, 1H), 4.05-4.00 (m, 2H), 3.81-3.77 (dd, *J* = 3.6 Hz, *J* = 10.8 Hz, 1H), 3.74-3.68 (m, 3H), 3.38 (m, 2H), 3.17-3.14 (m, 1H), 2.13-2.06 (m, 1H), 1.80-1.74 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.2, 139.0, 138.5, 138.2, 138.2, 137.7, 129.3, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.0, 127.7, 127.7, 127.7, 127.7, 127.7, 127.7, 127.6, 127.5, 119.5, 111.8, 98.3, 86.5, 83.6, 82.2, 78.3, 75.6, 75.4, 74.8, 73.4, 71.4, 68.8, 39.2, 36.2; HRMS (EI): *m*/*z* calcd for $C_{42}H_{44}INO_6$ (M^+) 785.2213, found 785.2219.

(1*S*,2*R*,3*S*,4*S*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-1-(2-(phenylamino)ethyl)tetrahydro-2H-pyran-1-ol (3m)



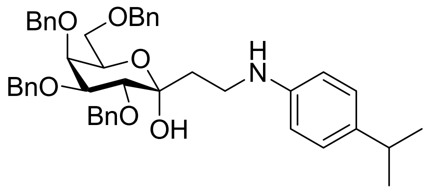
Compound **1b** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the pale yellow oil **3m** (48.6 mg, 82%): $[\alpha]^{25}_{D}$ +6.9 (c 0.43, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.24 (m, 20H), 7.14-7.10 (m, 2H), 6.76-6.72 (m, 1H), 6.62-6.60 (m, 2H), 4.97 (d, *J* = 11.2 Hz, 1H), 4.94 (d, *J* = 11.2 Hz, 1H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.70 (d, *J* = 11.6 Hz, 1H), 4.67 (d, *J* = 11.3 Hz, 1H), 4.62 (d, *J* = 11.3 Hz, 1H), 4.49 (d, *J* = 11.8 Hz, 1H), 4.46 (d, *J* = 11.8 Hz, 1H), 4.16 (dd, *J* = 6.4 Hz, *J* = 6.7 Hz, 1H), 4.01-3.96 (m, 2H), 3.84 (d, *J* = 9.4 Hz, 1H), 3.61-3.55 (m, 2H), 3.49-3.42 (m, 1H), 3.16-3.10 (m, 1H), 2.15-2.08 (m, 1H), 1.76-1.70 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.9, 138.8, 138.4, 138.1, 138.0, 129.1, 129.1, 128.6, 128.6, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.0, 128.0, 127.8, 127.8, 127.6, 127.5, 127.5, 127.5, 127.5, 118.7, 114.4, 114.4, 99.1, 80.8, 78.9, 75.5, 74.4, 74.4, 73.4, 72.4, 69.9, 69.0, 39.5, 35.7; HRMS (EI): *m*/*z* calcd for $C_{42}H_{45}NO_6$ (M^+) 659.3247, found 659.3252.

(1*S*,2*R*,3*S*,4*S*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-1-(2-(p-tolylamino)ethyl)tetrahydro-2H-pyran-1-ol (3n)



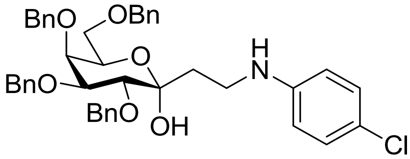
Compound **1b** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the pale yellow oil **3n** (46.0 mg, 76%): $[\alpha]^{25}_{D}$ +5.8 (c 0.75, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.24 (m, 20H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.56 (d, *J* = 8.0 Hz, 2H), 4.96 (d, *J* = 11.2 Hz, 1H), 4.94 (d, *J* = 12.0 Hz, 1H), 4.74 (d, *J* = 11.6 Hz, 1H), 4.70 (d, J = 11.6 Hz, 1H), 4.67 (d, J = 11.6 Hz, 1H), 4.62 (d, J = 11.6 Hz, 1H), 4.48 (d, J = 12.0 Hz, 1H), 4.44 (d, J = 12.0 Hz, 1H), 4.19-4.15 (m, 1H), 4.00-3.98 (m, 2H), 3.82 (d, $J_{2,3}$ = 9.6 Hz, 1H), 3.61-3.45 (m, 3H), 3.13-3.08 (m, 1H), 2.22 (s, 3H), 2.16-2.09 (m, 1H), 1.70-1.65 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.4, 138.8, 138.5, 138.2, 138.0, 129.6, 129.6, 128.6, 128.6, 128.4, 128.3, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.8, 127.8, 127.7, 127.6, 127.5, 127.5, 127.5, 114.9, 114.9, 99.1, 80.7, 79.1, 75.4, 74.6, 74.4, 73.4, 72.5, 69.8, 69.0, 40.2, 35.5, 20.4; HRMS (EI): *m/z* calcd for $C_{43}H_{47}NO_6$ (M^+) 673.3403, found 673.3409.

(1*S*,2*R*,3*S*,4*S*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-1-(2-((4-isopropylphenyl)amino)ethyl)tetrahydro-2H-pyran-1-ol (3o)



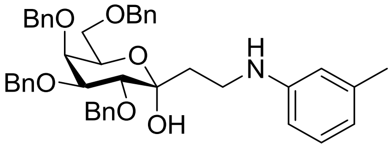
Compound **1b** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the pale yellow oil **3o** (49.8 mg, 79%): $[\alpha]^{25}_D$ +4.3 (c 0.37, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.25 (m, 20H), 6.99 (d, J = 8.4 Hz, 2H), 6.60 (d, J = 8.4 Hz, 2H), 4.97 (d, J = 11.2 Hz, 1H), 4.94 (d, J = 11.6 Hz, 1H), 4.75 (d, J = 11.6 Hz, 1H), 4.71 (d, J = 11.6 Hz, 1H), 4.67 (d, J = 11.2 Hz, 1H), 4.63 (d, J = 11.6 Hz, 1H), 4.49 (d, J = 11.6 Hz, 1H), 4.46 (d, J = 11.6 Hz, 1H), 4.18-4.15 (m, 1H), 4.00-3.98 (m, 2H), 3.82 (d, J = 9.6 Hz, 1H), 3.62-3.47 (m, 3H), 3.14-3.09 (m, 1H), 2.82-2.75 (m, 1H), 2.17-2.10 (m, 1H), 1.70-1.65 (m, 1H), 1.19 (d J = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.7, 139.6, 138.8, 138.5, 138.2, 138.1, 128.6, 128.6, 128.4, 128.3, 128.3, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 127.8, 127.7, 127.7, 127.6, 127.5, 127.5, 127.5, 127.4, 127.0, 126.9, 114.9, 114.9, 99.2, 80.7, 79.1, 75.4, 74.6, 74.4, 73.4, 72.5, 69.8, 69.1, 40.1, 35.4, 33.2, 24.1, 24.1; HRMS (EI): *m*/*z* calcd for $C_{45}H_{51}NO_6$ (M^+) 701.3716, found 701.3713.

(1*S*,2*R*,3*S*,4*S*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-1-(2-((4-chlorophenyl)amino)ethyl)tetrahydro-2H-pyran-1-ol (3p)



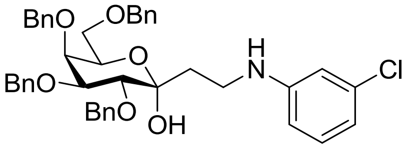
Compound **1b** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the pale yellow oil **3p** (48.0 mg, 77%): $[\alpha]^{25}_{D}$ +5.4 (c 0.40, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38-7.27 (m, 20H), 7.04-7.01 (m, 2H), 6.47-6.45 (m, 2H), 4.96 (d, *J* = 11.6 Hz, 1H), 4.93 (d, *J* = 11.6 Hz, 1H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.69 (d, *J* = 11.6 Hz, 1H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.60 (d, *J* = 11.6 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.16-4.13 (m, 1H), 4.05 (brs, 1H), 3.99 (dd, *J* = 0.8 Hz, *J* = 2.8 Hz, 1H), 3.96 (dd, *J* = 2.8 Hz, *J* = 9.6 Hz, 1H), 3.83 (d, *J* = 9.6 Hz, 1H), 3.57 (d, *J* = 6.4 Hz, 2H), 3.34-3.28 (m, 1H), 3.12-3.07 (m, 1H), 2.10-2.03 (m, 1H), 1.79-1.73 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ. 146.6, 138.7, 138.3, 138.0. 137.9, 128.9, 128.9, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.0, 128.0, 127.8, 127.8, 127.8, 127.7, 127.6, 127.5, 127.5, 127.5, 122.8, 115.0, 115.0, 99.0, 80.8, 78.5, 75.5, 74.4, 74.3, 73.4, 72.4, 70.0, 69.0, 39.5, 35.8; HRMS (EI): *m*/*z* calcd for $C_{42}H_{44}ClNO_6$ (M^+) 693.2857, found 693.2850.

(1*S*,2*R*,3*S*,4*S*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-1-(2-(m-tolylamino)ethyl)tetrahydro-2H-pyran-1-ol (3q)



(0.09 mmol, 51 mg) was treated according to the aforementioned method to give the pale yellow oil **3q** (59.7 mg, 71%): $[\alpha]^{25}_{D}$ -12.3 (c 0.31, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38-7.25 (m, 20H), 7.03-6.99 (m, 1H), 6.57 (d, *J* = 7.6 Hz, 1H), 6.44-6.43 (m, 2H), 4.96 (d, *J* = 10.8 Hz, 1H), 4.94 (d, *J* = 10.8 Hz, 1H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.70 (d, *J* = 11.6 Hz, 1H), 4.66 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 11.6 Hz, 1H), 4.49 (d, *J* = 11.6 Hz, 1H), 4.45 (d, *J* = 11.6 Hz, 1H), 4.18-4.14 (m, 1H), 4.00 (dd, *J* = 1.2 Hz, *J* = 2.8 Hz , 1H), 3.98 (dd, *J* = 2.8 Hz, *J* = 9.6, 1H), 3.83 (d, *J* = 9.6 Hz, 1H), 3.60 (dd, *J* = 7.2 Hz, *J* = 9.2 Hz , 1H), 3.56 (dd, *J* = 6.0 Hz, *J* = 9.2 Hz , 1H), 3.49-3.43 (m, 1H), 3.16-3.10 (m, 1H), 2.23 (s, 3H), 2.16-2.08 (m, 1H), 1.75-1.69 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.9, 138.8, 138.8, 138.4, 138.2, 138.0, 129.0, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.0, 128.0, 127.8, 127.7, 127.7, 127.6, 127.5, 127.5, 127.5, 127.5, 119.6, 115.1, 111.6, 99.1, 80.8, 79.0, 75.5, 74.5, 74.4, 73.4, 72.5, 69.9, 69.0, 39.6, 35.7, 21.5; HRMS (EI): *m/z* calcd for $C_{43}H_{47}NO_6$ (M^+) 673.3403, found 673.3408.

(1*S*,2*R*,3*S*,4*S*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-1-(2-((3-chlorophenyl)amino)ethyl)tetrahydro-2H-pyran-1-ol (3r)



Compound **1b** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the pale yellow oil **3r** (45.6 mg, 73%): $[\alpha]^{25}_{D}$ -0.3 (c 0.24, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.27 (m, 20H), 6.99 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 6.66

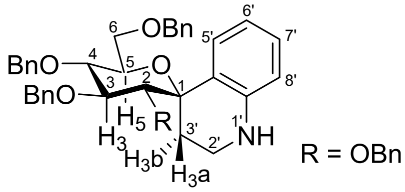
(d, *J* = 7.6 Hz, 1H), 6.53 (dd, *J* = 2.0 Hz, *J* = 2.0 Hz, 1H), 6.38 (dd, *J* = 2.0 Hz, *J* = 8.0 Hz, 1H), 4.96 (d, *J* = 11.6 Hz, 1H), 4.93 (d, *J* = 11.6 Hz, 1H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.67 (d, *J* = 11.6 Hz, 1H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.60 (d, *J* = 11.6 Hz, 1H), 4.49 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.14 (t, *J* = 6.8 Hz, 1H), 4.00 (brs, 1H), 3.94 (dd, *J* = 2.4 Hz, *J* = 9.6 Hz, 1H), 3.84 (d, *J* = 9.6 Hz, 1H), 3.57 (d, *J* = 6.4 Hz, 2H), 3.30-3.24 (m, 1H), 3.13-3.07 (m, 1H), 2.08-2.01 (m, 1H), 1.82-1.76 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ. 149.2, 138.6, 138.2, 137.9, 137.9, 134.8, 130.0, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.2, 128.2, 128.2, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.5, 127.5, 127.5, 117.8, 113.2, 112.2, 98.9, 80.9, 78.3, 75.5, 74.4, 74.1, 73.4, 72.3, 70.1, 69.9, 39.1, 35.9; HRMS (EI): *m*/*z* calcd for $C_{42}H_{44}ClNO_6$ (M^+) 693.2857, found 693.2850.

Typical Procedure for Synthesis of anomeric *s*piro-glycosides 4a-4y.

To a solution of exo-glycals **1** (0.09 mmol), arylamines (0.11 mmol) and acetic acid (0.68 mmol) in dichloroethane (DCE) (2.0 mL) was added $ZnCl_2$ (0.14 mmol). The reaction mixture was stirred at 55 ^oC under N_2 for 8 h. When the starting material complete transformed into product **3** (was determined by TLC), increasing temperature to 80 °C then added extra $ZnCl_2$ (0.09 mmol) for 8h. After the reaction was complete, CH_2Cl_2 (50 mL) was added to the reaction mixture, washed twice with H_2O (20 mL for each), twice with brine (20 mL for each), and dried over $MgSO_4$. The collected organic layer was concentrated under reduced pressure. Finally, the reaction mixture was purified by silica gel column chromatography with *n*-hexane/ethyl acetate (4/1) to give anomeric spiro-glycosides **4a-4y** in 60–90% yields.

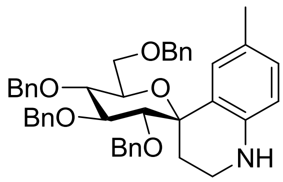
Spectroscopic Characterization Data of 4a-4y.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4a)[S1]



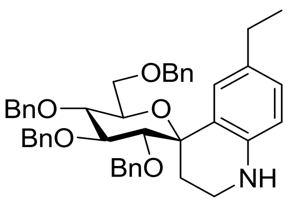
Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4a** (49.6 mg, 86%): $[\alpha]^{25}_{D}$ +44.2 (*c* 0.22, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 (2H, d, *J* = 8.0 Hz, ArH), 7.32-7.17 (18H, m, ArH), 7.06 (1H, dd, *J* = 7.2 Hz, *J* = 8.0 Hz, ArH), 6.99-6.98 (2H, m, ArH), 6.72 (1H, dd, *J* = 7.2 Hz, *J* = 7.6 Hz, ArH), 6.55 (1H, d, *J* = 8.0 Hz, ArH), 4.91 (1H, d, *J* = 10.4 Hz, CH_2Ph), 4.88 (1H, d, *J* = 10.8 Hz, CH_2Ph), 4.84 (1H, d, *J* = 10.8 Hz, CH_2Ph), 4.66-4.63 (2H, m, CH_2Ph), 4.51 (1H, d, *J* = 12.0 Hz, CH_2Ph), 4.41 (1H, d, *J* = 10.8 Hz, CH_2Ph), 4.04 (1H, d, *J* = 10.4 Hz, CH_2Ph), 3.96 (1H, d, *J* = 8.8 Hz, H2), 3.89 (1H, dd, *J* = 8.4 Hz, *J* = 8.8 Hz, H3), 3.84-3.77 (3H, m, H4, H5, H6a), 3.69 (1H, d, *J* = 10.4 Hz, H6b), 3.48-3.42 (1H, m, H2a'), 3.23-3.18 (1H, m, H2b'), 2.48-2.41 (1H, m, H3a'), 2.16-2.10 (1H, m, H3b'); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.2, 138.7, 138.6, 138.3, 138.3, 128.7, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7, 127.6, 127.5, 127.5, 127.3, 127.3, 123.5, 117.6, 114.9, 85.9 (C-2), 83.5 (C-3), 79.0 (C-4), 75.6 (*$PhCH_2$* at C-3), 75.1 (*$PhCH_2$* at C-4), 74.9 (*$PhCH_2$* at C-6), 74.2 (C-1), 73.4 (*$PhCH_2$* at C-2), 72.4 (C-5), 69.5 (C-6), 38.5 (C-2'), 26.3 (C-3'); HRMS (EI): *m/z* calcd for $C_{42}H_{43}NO_5$ (M^+) 641.3141, found 641.3133.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-6'-methyl-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4b)[S1]



Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4b** (48.3 mg, 82%): $[\alpha]^{25}_{D}$ +25.0 (*c* 0.23, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34-7.17 (m, 19H), 6.99-6.97 (m, 2H), 6.87 (dd, *J* = 1.6 Hz, *J* = 8.0 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 4.92 (d, *J* = 10.8 Hz, 1H), 4.88 (d, *J* = 10.8 Hz, 1H), 4.84 (d, *J* = 10.8 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 10.4 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.37 (d, *J* = 10.4 Hz, 1H), 4.05 (d, *J* = 10.8 Hz, 1H), 3.95 (d, *J* = 10.8 Hz, 1H), 3.89-3.76 (m, 4H), 3.69 (d, *J* = 10.4 Hz, 1H), 3.44-3.39 (m, 1H), 3.20-3.14 (m, 1H), 2.46-2.40 (m, 1H), 2.21 (s, 3H), 2.15-2.08 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.9, 138.8, 138.6, 138.3, 138.2, 129.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.0, 128.0, 128.0, 128.0, 128.0, 128.0, 128.0, 127.7, 127.6, 127.6, 127.5, 127.5, 127.5, 127.3, 127.3, 126.7, 123.6, 115.1, 85.7, 83.5, 79.0, 75.5, 75.1, 74.7, 74.3, 73.3, 72.3, 69.5, 38.7, 26.5, 20.7; HRMS (EI): *m*/*z* calcd for $C_{43}H_{45}NO_5$ (M^+) 655.3298, found 655.3306.

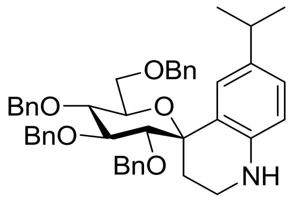
(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-6'-ethyl-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4c)[S1]



Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4c** (45.8 mg, 76%): $[\alpha]^{25}_{D}$ +20.5 (*c* 0.34, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34-7.17 (m, 19H), 6.99-6.96 (m, 2H), 6.90 (dd, *J* = 2.0 Hz, *J* = 8.0 Hz, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 4.91 (d, *J* = 10.8 Hz, 1H), 4.89 (d, *J* = 10.0 Hz, 1H), 4.85 (d, *J* = 10.8 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.65 (d, *J* = 10.6 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.38 (d, *J* = 10.6 Hz, 1H), 4.03 (d, *J* = 10.6 Hz, 1H), 3.98 (d,

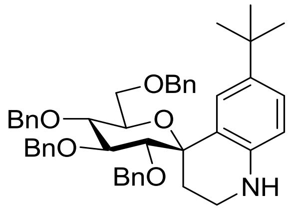
J = 9.4 Hz, 1H), 3.90-3.76 (m, 4H), 3.69 (dd, J = 10.8 Hz, J = 1.6 Hz, 1H), 3.44-3.38 (m, 1H), 3.21-3.15 (m, 1H), 2.52 (q, J = 7.6 Hz, 2H), 2.48-2.39 (m, 1H), 2.16-2.10 (m, 1H), 1.15 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.2, 138.7, 138.6, 138.3, 138.3, 133.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.0, 128.0, 128.0, 128.0, 127.9, 127.9, 127.7, 127.7, 127.7, 127.5, 127.4, 127.4, 127.3, 127.3, 126.8, 123.5, 115.2, 85.8, 83.5, 79.0, 75.6, 75.1, 74.8, 74.4, 73.3, 72.3, 69.4, 38.6, 28.2, 26.4, 16.0; HRMS (EI): *m*/*z* calcd for $C_{44}H_{47}NO_5$ (M^+) 669.3454, found 669.3445.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-6'-isopropyl-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4d)[S1]



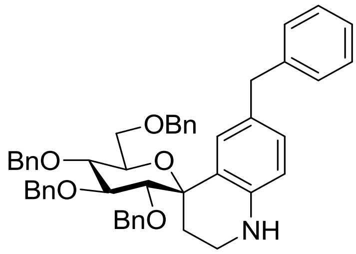
Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4d** (46.0 mg, 75%): $[\alpha]^{25}_{D}$ +29.2 (*c* 0.22, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.18 (m, 19H), 6.98-6.92 (m, 3H), 6.52 (d, J = 8.2 Hz, 1H), 4.92 (d, J = 10.8 Hz, 1H), 4.91 (d, J = 10.8 Hz, 1H), 4.85 (d, J = 10.8 Hz, 1H), 4.69 (d, J = 12.0 Hz, 1H), 4.68 (d, J = 10.8 Hz, 1H), 4.51 (d, J = 12.0 Hz, 1H), 4.39 (d, J = 10.4 Hz, 1H), 4.01 (d, J = 10.4 Hz, 1H), 4.00 (d, J = 6.8 Hz, 1H), 3.90-3.83 (m, 3H), 3.79-3.76 (m, 1H), 3.70 (d, J = 10.4 Hz, 1H), 3.43-3.37 (m, 1H), 3.21-3.15 (m, 1H), 2.81-2.74 (m, 1H), 2.45-2.39 (m, 1H), 2.17-2.10 (m, 1H), 1.17 (d, J = 6.8 Hz, 3H), 1.16 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.3, 138.7, 138.7, 138.4, 138.3, 138.1, 128.4, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.5, 127.4, 127.4, 127.3, 127.3, 126.9, 125.3, 123.3, 115.1, 85.9, 83.5, 79.0, 75.6, 75.2, 74.9, 74.4, 73.3, 72.4, 69.4, 38.6, 33.4, 26.3, 24.4, 24.1; HRMS (EI): *m/z* calcd for $C_{45}H_{49}NO_5$ (M^+) 683.3611, found 683.3614.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-6'-(tert-butyl)-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4e)[S1]



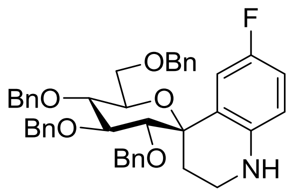
Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4e** (51.0 mg, 60%):$[\alpha]^{25}_D$ +39.5 (*c* 0.23, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53 (d, *J* = 2.4 Hz, 1H), 7.33-7.18 (m, 18H), 7.10 (dd, *J* = 2.0 Hz, *J* = 8.4 Hz, 1H), 6.98-6.96 (m, 2H), 6.53 (d, *J* = 8.4 Hz, 1H), 4.91 (d, *J* = 10.8 Hz, 2H), 4.85 (d, *J* = 10.4 Hz, 1H), 4.70 (d, *J* = 10.8 Hz, 2H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.40 (d, *J* = 10.4 Hz, 1H), 4.00-3.98 (m, 2H), 3.95-3.85 (m, 3H), 3.79-3.77 (m, 1H), 3.70 (m, 1H), 3.43-3.38 (m, 1H), 3.22-3.16 (m, 1H), 2.46-2.39 (m, 1H), 2.18-2.11 (m, 1H), 1.24 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.9, 140.3, 138.7, 138.6, 138.4, 138.3, 128.4, 128.4, 128.4, 128.4, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.9, 127.7, 127.6, 127.3, 127.3, 127.3, 127.2, 125.8, 124.2, 122.8, 114.9, 86.0, 83.5, 79.0, 75.7, 75.2, 74.9, 74.5, 73.3, 72.5, 69.3, 38.6, 34.0, 31.5, 31.5, 31.5, 26.33; HRMS (EI): *m/z* calcd for $C_{46}H_{51}NO_5$ (M^+) 697.3767, found 697.3773.

(1*S*,2*R*,3*S*,4*R*,5*R*)-6'-benzyl-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4f)



Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4e** (51.0 mg, 65%): $[\alpha]^{25}_{D}$ -29.0 (*c* 0.21, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34-7.08 (m, 24H), 6.96-6.93 (m, 2H), 6.88 (dd, *J* = 1.6 Hz, *J* = 8.0 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 4.89 (d, *J* = 10.8 Hz, 1H), 4.88 (d, *J* = 10.8 Hz, 1H), 4.82 (d, *J* = 10.8 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 2H), 4.49 (d, *J* = 12.0 Hz, 1H), 4.34 (d, *J* = 10.8 Hz, 1H), 3.97 (d, *J* = 10.8 Hz, 1H), 3.93-3.77 (m, 7H), 3.68 (d, *J* = 10.0 Hz, 1H), 3.43-3.37 (m, 1H), 3.22-3.17 (m, 1H), 2.47-2.37 (m, 1H), 2.17-2.11 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.5, 142.1, 138.6, 138.6, 138.4, 138.2, 130.0, 129.5, 128.6, 128.6, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.2, 128.2, 128.1, 128.0, 128.0, 128.0, 128.0, 127.8, 127.8, 127.7, 127.7, 127.7, 127.5, 127.5, 127.5, 127.3, 127.3, 125.7, 123.4, 115.3, 85.6, 83.5, 79.0, 75.6, 75.1, 74.9, 74.3, 73.3, 72.3, 69.4, 41.3, 38.4, 26.1; HRMS (EI): *m*/*z* calcd for $C_{49}H_{49}NO_5$ (M^+) 731.3611, found 731.3613.

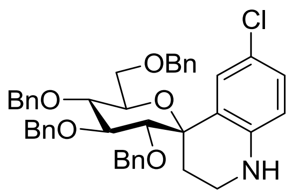
(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-6'-fluoro-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4g)[S1]



Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4g** (46.8 mg, 79%): $[\alpha]^{25}_{D}$ +42.7 (*c* 0.25, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.19 (m, 19H), 6.98 (m, 2H), 6.82-6.78 (m, 1H), 6.51-6.47

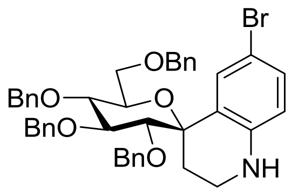
(m, 1H), 4.91 (d, *J* = 11.2 Hz, 1H), 4.87 (d, *J* = 11.2 Hz, 1H), 4.84 (d, *J* = 11.2 Hz, 1H), 4.62 (m, 2H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 10.4 Hz, 1H), 4.08 (d, *J* = 10.4 Hz, 1H), 3.88-3.82 (m, 3H), 3.78-3.76 (m, 2H), 3.68 (d, *J* = 10.4 Hz, 1H), 3.48-3.44 (m, 1H), 3.19-3.14 (m, 1H), 2.46-2.41 (m, 1H), 2.11-2.06 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.7 (d, *J* = 233.4 Hz), 142.6, 138.6, 138.4, 138.2, 138.1, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.6, 127.6, 127.5, 127.4, 127.4, 124.7 (d, *J* = 5.8 Hz), 115.9 (d, *J* = 22.4 Hz), 115.8 (d, *J* = 5.8 Hz), 113.7 (d, *J* = 22.4 Hz), 85.9, 83.4, 78.9, 75.5, 75.1, 75.0, 74.2, 73.3, 72.5, 69.5, 38.7, 26.3; HRMS (EI): *m/z* calcd for $C_{42}H_{42}FNO_5$ (M^+) 659.3047, found 659.3054.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-6'-chloro-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4h)



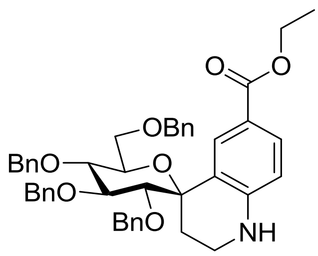
Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4h** (42.5 mg, 70%): $[\alpha]^{25}_{D}$ +19.5 (*c* 0.24, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 (d, *J* = 2.4 Hz, 1H), 7.33-7.25 (m, 14H), 7.19 (m, 4H), 7.01-6.99 (m, 3H), 6.47 (d, *J* = 8.6 Hz, 1H), 4.91 (d, *J* = 11.2 Hz, 1H), 4.86 (d, *J* = 10.8 Hz, 1H), 4.85 (d, *J* = 11.2 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 10.8 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 10.4 Hz, 1H), 4.09 (d, *J* = 10.4 Hz, 1H), 3.86-3.84 (m, 2H), 3.80-3.76 (m, 3H), 3.69-3.67 (m, 1H), 3.51-3.46 (m, 1H), 3.19 (m, 1H), 2.46-2.41 (m, 1H), 2.10-2.05 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.6, 138.7, 138.4, 138.1, 138.0, 128.7, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.3, 128.1, 128.1, 128.0, 128.0, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 127.5, 127.4, 127.4, 127.4, 124.9, 122.0, 115.9, 85.8, 83.4, 78.9, 75.5, 75.1, 75.0, 74.0, 73.3, 72.5, 69.4, 38.5, 26.3; HRMS (EI): *m*/*z* calcd for $C_{42}H_{42}ClNO_5$ (M^+) 675.2752, found 675.2759.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-6'-bromo-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4i)



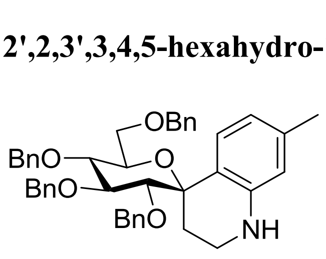
Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4i** (47.2 mg, 73%): $[\alpha]^{25}_D$ +6.6 (*c* 0.41, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.57 (d, *J* = 2.0 Hz, 1H), 7.35-7.18 (m, 18H), 7.14-7.11 (m, 1H), 7.00-6.97 (m, 2H), 6.41 (d, *J* = 8.4 Hz, 1H), 4.91 (d, *J* = 11.2 Hz, 1H), 4.86 (d, *J* = 10.8 Hz, 1H), 4.84 (d, *J* = 10.8 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 10.8 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 10.8 Hz, 1H), 4.09 (d, *J* = 10.8 Hz, 1H), 3.87-3.86 (m, 2H), 3.78-3.76 (m, 3H), 3.68 (m, 1H), 3.51-3.45 (m, 1H), 3.21-3.15 (m, 1H), 2.46-2.40 (m, 1H), 2.10-2.03 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.0, 138.7, 138.4, 138.1, 138.0, 131.4, 130.3, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.7, 127.6, 127.6, 127.5, 127.5, 127.5, 127.5, 127.4, 125.4, 116.3, 109.0, 85.8, 83.3, 78.9, 75.4, 75.1, 75.0, 73.9, 73.3, 72.5, 69.4, 38.4, 26.2; HRMS (EI): *m*/*z* calcd for $C_{42}H_{42}BrNO_5$ (M^+) 719.2246, found 719.2248.

(1*S*,2*R*,3*S*,4*R*,5*R*)-ethyl-2,3,4-tris(benzyloxy)-6-((benzyloxy)methyl)-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline]-6'-carboxylate (4j)



Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4j** (44.3 mg, 69%): $[\alpha]^{25}_{D}$ +18.2 (*c* 0.17, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.2 (d, *J* = 2.0 Hz, 1H), 7.75 (dd, *J* = 2.0 Hz, *J* = 8.4 Hz, 1H), 7.35-7.16 (m, 18H), 6.98-6.95 (m, 2H), 6.49 (d, *J* = 8.4 Hz, 1H), 4.92 (d, *J* = 10.8 Hz, 1H), 4.88 (d, *J* = 10.8 Hz, 1H), 4.87 (d, *J* = 10.6 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 10.6 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 10.6 Hz, 1H), 4.39 (brs, 1H), 4.28 (q, *J* = 7.2, 1H), 4.11 (d, *J* = 10.6 Hz, 1H), 4.05 (d, *J* = 9.6 Hz, 1H), 3.92 (dd, *J* = 8.0 Hz, *J* = 9.6 Hz, 1H),3.84-3.68 (m, 4H), 3.57-3.51 (m, 1H), 3.31-3.25 (m, 1H), 2.48-2.41 (m, 1H), 2.15-2.08 (m, 1H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.7, 149.6, 138.6, 138.5, 138.1, 138.1, 130.6, 129.8, 128.4, 128.4, 128.4, 128.4, 128.4, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.8, 127.7, 127.7, 127.7, 127.7, 127.6, 127.6, 127.4, 127.3, 122.1, 118.7, 113.8, 85.4, 83.6, 79.1, 75.6, 75.3, 75.3, 73.9, 73.4, 72.6, 69.5, 60.1, 37.9, 25.7, 14.4; HRMS (EI): *m/z* calcd for $C_{45}H_{47}NO_7$ (M^+) 713.3353, found 713.3349.

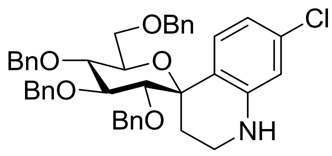
(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-7'-methyl-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4k)[S1]



Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4k** (47.8 mg, 81%): $[\alpha]^{25}_{D}$ +20.0 (*c* 0.19, $CHCl_3$); ^1H NMR

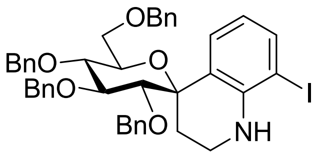
(CDCl$_3$, 400 MHz) δ 7.36-7.18 (m, 19H), 7.00 (m, 2H), 6.54 (d, *J* = 8.0 Hz, 1H), 6.37 (brs, 1H), 4.90 (d, *J* = 10.0 Hz, 1H), 4.88 (d, *J* = 8.8 Hz, 1H), 4.83 (d, *J* = 11.2 Hz, 1H), 4.70 (brs, 1H), 4.64 (d, *J* = 11.6 Hz, 2H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.41 (d, *J* = 10.4 Hz, 1H), 4.10 (d, *J* = 10.4 Hz, 1H), 3.96 (d, *J* = 9.6 Hz, 1H), 3.87 (dd, *J* = 8.8 Hz, *J* = 9.6 Hz, 1H), 3.83-3.74 (m, 3H), 3.68 (d, *J* = 10.4 Hz, 1H), 3.43-3.39 (m, 1H), 3.22-3.17 (m, 1H), 2.47-2.39 (m, 1H), 2.22 (s, 3H), 2.16-2.09 (m, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 146.1, 138.7, 138.6, 138.5, 138.5, 138.3, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.0, 128.0, 128.0, 128.0, 127.9, 127.9, 127.7, 127.7, 127.6, 127.6, 127.6, 127.6, 127.5, 127.3, 127.3, 120.8, 118.9, 115.4, 85.6, 83.6, 79.0, 75.6, 75.1, 74.9, 74.2, 73.4, 72.3, 69.6, 38.5, 26.3, 21.1; HRMS (EI): *m*/*z* calcd for $C_{43}H_{45}NO_5$ (M^+) 655.3298, found 655.3291.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-7'-chloro-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4l)[S1]



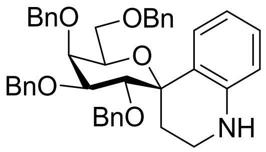
Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4l** (48.6 mg, 80%): $[\alpha]^{25}_D$ +29.2 (*c* 0.23, CHCl$_3$); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.36-7.19 (m, 19H), 7.01-6.98 (m, 2H), 6.64 (dd, *J* = 2.0 Hz, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 2.0 Hz, 1H), 4.92-4.83 (m, 3H), 4.63-4.60 (d, *J* = 12.0 Hz, 2H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 10.8 Hz, 1H), 4.11 (d, *J* = 10.8 Hz, 1H), 4.00 (brs, 1H), 3.89-3.73 (m, 5H), 3.67 (m, 1H), 3.51-3.45 (m, 1H), 3.23-3.17 (m, 1H), 2.46-2.40 (m, 1H), 2.12-2.05 (m, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 147.0, 138.6, 138.4, 138.1, 138.1, 134.1, 128.9, 128.4, 128.4, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.5, 127.5, 127.4, 121.9, 117.5, 114.0, 85.7, 83.4, 78.9, 75.6, 75.18, 75.11, 73.9, 73.3, 72.4, 69.4, 38.3, 26.1; HRMS (EI): *m/z* calcd for $C_{42}H_{42}ClNO_5$ (M^+) 675.2752, found 675.2744.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-8'-iodo-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4m)



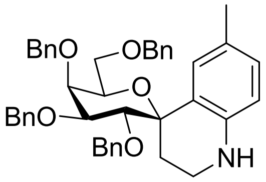
Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4m** (55.2 mg, 80%): $[\alpha]^{25}_{D}$ +68.4 (*c* 0.23, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58 (dd, *J* = 1.2 Hz, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.32-7.20 (m, 18H), 6.94-6.91 (m, 2H), 6.46 (d, *J* = 8.0 Hz, 1H), 4.92 (d, *J* = 10.8 Hz, 1H), 4.88 (d, *J* = 10.8 Hz, 1H), 4.86 (d, *J* = 10.8 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 2H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 10.4 Hz, CH_2Ph, 2H), 3.98 (d, *J* = 10.4 Hz, 1H), 3.90-3.88 (m, 2H), 3.81-3.75 (m, 3H), 3.69-3.67 (m, 1H), 3.58-3.53 (m, 1H), 3.27-3.24 (m, 1H), 2.47-2.41 (m, 1H), 2.11-2.04 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.2, 138.6, 138.6, 138.4, 138.1, 138.0, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.0, 128.0, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.4, 124.4, 118.5, 86.3, 84.9, 83.4, 78.9, 75.6, 75.3, 75.1, 74.4, 73.4, 72.6, 69.4, 38.6, 26.3; HRMS (EI): *m/z* calcd for $C_{42}H_{42}INO_5$ (M^+) 767.2108, found 767.2115.

(1*S*,2*R*,3*S*,4*S*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4n)[S1]



Compound **1b** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4n** (44.4 mg, 77%): $[\alpha]^{25}_{D}$ +28.9 (*c* 0.44, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.53 (dd, *J* = 1.2 Hz, *J* = 8.0 Hz, 1H), 7.41-7.24 (m, 15H), 7.17-7.14 (m, 3H), 7.05-7.01 (m, 1H), 6.99-6.96 (m, 2H), 6.72-6.68 (m, 1H), 6.53 (dd, *J* = 1.2 Hz, *J* = 8.0 Hz, 1H), 5.05 (d, *J* = 11.6 Hz, 1H), 4.75 (brs, 2H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.50 (d, *J* = 10.0 Hz, 1H), 4.49 (m, 1H), 4.43 (d, *J* = 11.6 Hz, 1H), 4.38 (d, *J* = 11.6 Hz, 1H), 4.10-4.07 (m, 2H), 3.88-3.84 (m, 1H), 3.75 (dd, *J* = 2.8 Hz, *J* = 10.0 Hz, 1H), 3.70 (dd, *J* = 8.0 Hz, *J* = 8.8 Hz, 1H), 3.51 (dd, *J* = 4.8 Hz, *J* = 8.8 Hz, 1H), 3.36-3.30 (m, 1H), 3.19-3.13 (m, 1H), 2.43-2.36 (m, 1H), 2.11-2.05 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.2, 139.3, 138.7, 138.7, 137.9, 128.6, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 127.9, 127.9, 127.9, 127.9, 127.9, 127.9, 127.9, 127.7, 127.4, 127.4, 127.3, 127.3, 127.3, 127.2, 127.1, 124.1, 117.9, 114.9, 81.7, 80.8, 75.2, 75.1, 75.0, 74.5, 73.5, 72.5, 70.4, 69.1, 38.6, 25.4; HRMS (EI): *m/z* calcd for $C_{42}H_{43}NO_5$ (M^+) 641.3141, found 641.3151.

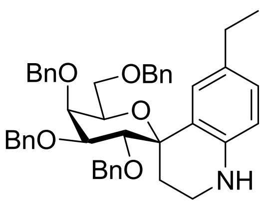
(1*S*,2*R*,3*S*,4*S*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-6'-methyl-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4o)[S1]



Compound **1b** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4o** (37.7 mg, 64%): $[\alpha]^{25}_{D}$ +11.5 (*c* 0.31, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.43-7.41 (m, 2H), 7.37-7.24 (m, 14H), 7.17-7.15 (m, 3H), 7.00-6.97 (m, 2H), 6.84 (dd, *J* = 1.6 Hz, *J* = 8.0 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 5.08 (d, *J*

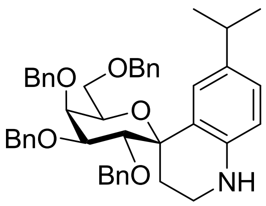
= 11.6 Hz, 1H), 4.75 (brs, 2H), 4.66 (d, *J* = 11.6 Hz, 1H), 4.51-4.37 (m, 4H), 4.11-4.09 (m, 2H), 3.86-3.83 (m, 1H), 3.76-3.68 (m, 2H), 3.51 (dd, *J* = 4.8 Hz, *J* = 8.8 Hz, 1H), 3.33-3.27 (m, 1H), 3.16-3.10 (m, 1H), 2.42-2.36 (m, 1H), 2.19 (s, 3H), 2.09-2.03 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.0, 139.5, 138.8, 138.6, 137.9, 129.4, 128.5, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.9, 127.7, 127.3, 127.3, 127.3, 127.2, 127.2, 127.1, 127.1, 126.9, 124.1, 115.1, 81.5, 80.9, 75.1, 75.0, 74.9, 74.2, 73.5, 72.5, 70.3, 69.1, 38.8, 25.6, 20.7; HRMS (EI): *m*/*z* calcd for $C_{43}H_{45}NO_5$ (M^+) 655.3298, found 655.3304.

(1*S*,2*R*,3*S*,4*S*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-6'-ethyl-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4p)[S1]



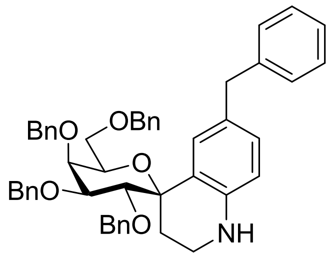
Compound **1b** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4p** (39.1 mg, 65%): $[\alpha]^{25}_D$ +22.8 (*c* 0.24, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43-7.24 (m, 16H), 7.16-7.15 (m, 3H), 6.98-6.96 (m, 2H), 6.88 (dd, *J* = 1.6 Hz, *J* = 8.0 Hz, 1H), 6.49 (dd, *J* = 8.0 Hz, 1H), 5.09 (d, *J* = 12.0 Hz, 1H), 4.76 (brs, 2H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.53 (d, J = 10.0 Hz, 1H), 4.47-4.37 (m, 3H), 4.10-4.06 (m, 2H), 3.87-3.84 (m, 1H), 3.76-3.68 (m, 2H), 3.51 (dd, *J* = 4.8 Hz, *J* = 8.8 Hz, 1H), 3.32-3.27 (m, 1H), 3.17-3.12 (m, 1H), 2.54-2.46 (m, 2H), 2.42-2.35 (m, 1H), 2.10-2.04 (m, 1H), 1.15 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.2, 139.5, 138.8, 138.7, 137.9, 133.5, 128.3, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 127.9, 127.9, 127.9, 127.9, 127.9, 127.9, 127.9, 127.7, 127.3, 127.3, 127.2, 127.1, 127.1, 127.1, 127.0, 124.1, 115.1, 81.7, 80.8, 75.2, 75.0, 74.9, 74.2, 73.5, 72.5, 70.3, 69.0, 38.7, 28.1, 25.4, 15.7; HRMS (EI): *m*/*z* calcd for $C_{44}H_{47}NO_5$ (M^+) 669.3454, found 669.3458.

(1*S*,2*R*,3*S*,4*S*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-6'-isopropyl-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4q)



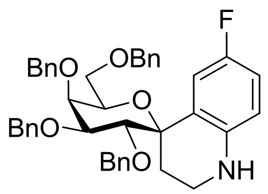
Compound **1b** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4q** (41.2 mg, 67%): $[\alpha]^{25}_{D}$ -6.2 (*c* 0.28 HCl3) ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45-7.15 (m, 19H), 6.96-6.91 (m, 3H), 6.51 (d, *J* = 8.0 Hz, 1H), 5.10 (d, *J* = 11.6 Hz, 1H), 4.76 (brs, 2H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.55 (d, *J* = 10.0 Hz, 1H), 4.47-4.38 (m, 3H), 4.10 (brs, 1H), 4.03 (d, *J* = 10.4 Hz, 1H), 3.88-3.85 (m, 1H), 3.75-3.69 (m, 2H), 3.54-3.51 (m, 1H), 3.29-3.27 (m, 1H), 3.17-3.12 (m, 1H), 2.81-2.74 (m, 1H), 2.41-2.35 (m, 1H), 2.10-2.06 (m, 1H), 1.17 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.3, 139.6, 138.8, 138.7, 138.2, 137.9, 128.3, 128.3, 128.3, 128.3, 128.2, 128.1, 128.1, 127.9, 127.9, 127.9, 127.9, 127.9, 127.7, 127.3, 127.3, 127.3, 127.1, 127.0, 126.9, 126.9, 126.8, 125.9, 123.9, 115.1, 81.9, 80.8, 75.2, 75.1, 75.0, 74.1, 73.5, 72.5, 70.3, 69.0, 38.7, 33.3, 25.4, 24.3, 23.9; HRMS (EI): *m*/*z* calcd for $C_{45}H_{49}NO_5$ (M^+) 683.3611, found 683.3614.

(1*S*,2*R*,3*S*,4*S*,5*R*)-6'-benzyl-3,4,5-tris(benzyloxy)-5-((benzyloxy)methyl)-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4r)



Compound **1b** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4r** (43.6 mg, 80%): $[\alpha]^{25}_{D}$ -27.1 (*c* 0.26, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41-7.39 (m, 3H), 7.35-7.25 (m, 13H), 7.19-7.08 (m, 8H), 6.95-6.93 (m, 2H), 6.83 (dd, *J* = 2.0 Hz, *J* = 8.0 Hz, 1H), 6.48 (d, *J* = 8.0 Hz, 1H), 5.05 (d, *J* = 12.0 Hz, 1H), 4.73 (brs, 2H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.47 (d, *J* = 10.0 Hz, 1H), 4.43 (d, *J* = 12.0 Hz, 1H), 4.42 (d, *J* = 10.8 Hz, 1H), 4.38 (d, *J* = 11.6 Hz, 1H), 4.07 (d, *J* = 2.8 Hz, 1H), 3.98 (d, *J* = 10.8 Hz, 1H), 3.88-3.79 (m, 3H), 3.73 (dd, *J* = 2.8 Hz, *J* = 10.0 Hz, 1H), 3.69 (dd, *J* = 8.4 Hz, *J* = 8.8 Hz, 1H), 3.51 (dd, *J* = 4.8 Hz, *J* = 8.8 Hz, 1H), 3.31-3.26 (m, 1H), 3.19-3.13 (m, 1H), 2.39-2.32 (m, 1H), 2.11-2.05 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.5, 142.2, 139.4, 138.8, 138.7, 137.9, 130.1, 129.3, 128.7, 128.6, 128.6, 128.3, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.1, 127.9, 127.9, 127.9, 127.9, 127.7, 127.7, 127.7, 127.3, 127.3, 127.3, 127.3, 127.2, 127.1, 127.1, 125.6, 123.9, 115.3, 81.4, 80.8, 75.1, 75.1, 74.9, 74.3, 73.5, 72.5, 70.3, 69.0, 41.3, 38.5, 25.1; HRMS (EI): *m/z* calcd for $C_{49}H_{49}NO_5$ (M^+) 731.3611, found 731.3607.

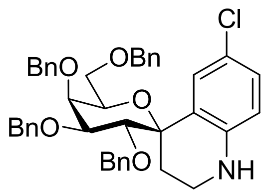
(1*S*,2*R*,3*S*,4*S*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-6'-fluoro-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4s)[S1]



Compound **1b** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4s** (48.1 mg. 81%): $[\alpha]^{25}_{D}$ +15.4 (*c* 0.61, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.16 (m, 19H), 7.00-6.98 (m, 2H), 6.79-6.74 (m, 1H), 6.46

(dd, J = 4.8 Hz, J = 8.8 Hz, 1H), 5.04 (d, J = 11.8 Hz, 1H), 4.74 (brs, 2H), 4.64 (d, J = 11.8 Hz, 1H), 4.53 (d, J = 10.8 Hz, 1H), 4.45-4.37 (m, 3H), 4.12 (d, J = 10.8 Hz, 1H), 4.06 (d, J = 2.8 Hz, 1H), 3.85-3.82 (m, 1H), 3.74 (dd, J = 2.8 Hz, J = 10.0 Hz, 1H), 3.68 (dd, J = 8.4 Hz, J = 8.8 Hz, 1H), 3.50 (dd, J = 5.2 Hz, J = 8.8 Hz, 1H), 3.36-3.31 (m, 1H), 3.15-3.09 (m, 1H), 2.42-2.35 (m, 1H), 2.07-2.01 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.8 (d, J = 233.2 Hz), 142.6, 139.2, 138.6, 138.4, 137.9, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.7, 127.4, 127.4, 127.4, 127.3, 127.3, 127.3, 127.2, 125.3 (d, J = 6.1 Hz), 115.8 (d, J = 11.6 Hz), 115.8 (d, J = 3.6 Hz), 114.2 (d, J = 22.4 Hz), 81.6, 80.7, 75.2, 75.0, 74.9, 74.5, 73.5, 72.5, 70.6, 69.0, 38.9, 25.5; HRMS (EI): m/z calcd for $C_{42}H_{42}FNO_5$ (M^+) 659.3047, found 659.3043.

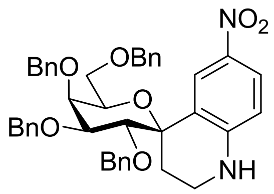
(1*S*,2*R*,3*S*,4*S*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-6'-chloro-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4t)[S1]



Compound **1b** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4t** (45.0 mg, 74%): $[\alpha]^{25}_{D}$ -15.0 (c 0.42, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 (d, J = 2.4 Hz, 1H), 7.41-7.24 (m, 15H), 7.19-7.17 (m, 3H), 7.01-6.96 (m, 3H), 6.45 (d, J = 8.4 Hz, 1H), 5.05 (d, J = 12.0 Hz, 1H), 4.74 (brs, 2H), 4.65 (d, J = 12.0 Hz, 1H), 4.54 (d, J = 10.8 Hz, 1H), 4.44-4.37 (m, 3H), 4.13 (d, J = 10.8 Hz, 1H), 4.06 (d, J = 2.8 Hz, 1H), 3.92 (brs, 1H), 3.84-3.81 (m, 1H), 3.64 (dd, J = 2.8 Hz, J = 10.0 Hz, 1H), 3.67 (dd, J = 8.0 Hz, J = 8.8 Hz, 1H), 3.50 (dd, J = 5.2 Hz, J = 8.8 Hz, 1H), 3.39-3.34 (m, 1H), 3.17-3.11 (m, 1H), 2.42-2.35 (m, 1H), 2.05-2.00 (m, 1H); ^{13}C

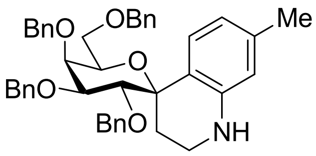
NMR ($CDCl_3$, 100 MHz) δ 144.7, 139.2, 138.6, 138.4, 137.9, 128.6, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 128.0, 128.0, 128.0, 127.9, 127.9, 127.9, 127.9, 127.9, 127.7, 127.4, 127.4, 127.4, 127.3, 127.3, 127.2, 125.5, 122.2, 116.0, 81.6, 80.7, 75.2, 74.8, 74.7, 74.3, 73.5, 72.5, 70.7, 69.0, 38.6, 25.4; HRMS (EI): *m*/*z* calcd for $C_{42}H_{42}ClNO_5$ (M^+) 675.2752, found 675.2744.

(1*S*,2*R*,3*S*,4*S*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-6'-nitro-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4u)



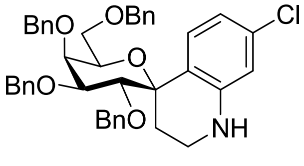
Compound **1b** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4u** (55.6 mg. 90%): $[\alpha]^{25}_D$ -36.0 (c 0.60, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.39 (d, *J* = 2.4 Hz, 1H), 7.89 (dd, *J* = 2.4 Hz, *J* = 9.2 Hz, 1H), 7.43-7.23 (m, 15H), 7.17-7.10 (m, 3H), 6.96-6.93 (m, 2H), 6.39 (d, *J* = 9.2 Hz, 1H), 5.07 (d, *J* = 12.0 Hz, 1H), 4.79 (d, *J* = 11.6 Hz, 1H), 4.74-4.71 (m, 2H), 4.69-4.65 (m, 2H), 4.50 (d, *J* = 10.0 Hz, 1H), 4.41 (d, *J* = 11.6 Hz, 1H), 4.37 (d, *J* = 11.6 Hz, 1H), 4.24 (d, *J* = 11.2 Hz, 1H), 4.08 (d, *J* = 2.0 Hz, 1H), 3.83-3.80 (m, 2H), 3.63 (dd, J = 7.6 Hz, J = 9.2 Hz, 1H), 3.55-3.48 (m, 2H), 3.30-3.24 (m, 1H), 2.44-2.37 (m, 1H), 2.06-1.99 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.9, 138.9, 138.3, 138.0, 137.9, 137.8, 128.4, 128.3, 128.3, 128.3, 128.3, 128.3, 128.0, 128.0, 127.9, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.5, 127.3, 127.3, 127.3, 127.3, 125.2, 125.1, 122.5, 113.3, 80.9, 80.72, 75.4, 74.3, 74.3, 74.2, 73.5, 72.3, 71.2, 69.1, 38.1, 24.7. HRMS (EI) *m*/*z* calcd for $C_{42}H_{42}N_2O_7$ (M^+) 686.2992, found 686.2997.

(1*S*,2*R*,3*S*,4*S*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-7'-methyl-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4v)[S1]



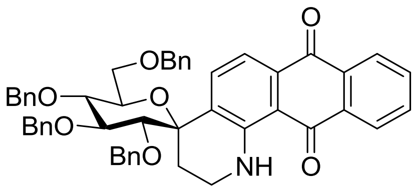
Compound **1b** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4v** (38.3 mg. 65%): $[\alpha]^{25}_{D}$ +20.6 (*c* 0.43, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41-7.16 (19H, m, ArH), 7.01-6.99 (m, 2H), 6.51 (d, *J* = 7.6 Hz, 1H), 6.35 (m, 1H), 5.05 (d, *J* = 12.0 Hz, 1H), 4.74 (brs, 2H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.51-4.48 (brs, 2H), 4.42 (d, *J* = 11.6 Hz, 1H), 4.37 (d, *J* = 11.6 Hz, 1H), 4.13 (d, *J* = 10.8 Hz, 1H), 4.06 (d, *J* = 2.4 Hz, 1H), 3.85-3.82 (m, 1H), 3.74 (dd, *J* = 2.4 Hz, *J* = 10.0 Hz, 1H), 3.69 (dd, *J* = 8.4 Hz, *J* = 8.8 Hz, 1H), 3.49 (dd, *J* = 4.8 Hz, *J* = 8.8 Hz, 1H), 3.32-3.27 (m, 1H), 3.19-3.13 (m, 1H), 2.41-2.34 (m, 1H), 2.20 (s, 3H), 2.09-2.03 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.1, 139.4, 138.8, 138.8, 138.3, 137.9, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.1, 127.9, 127.9, 127.9, 127.9, 127.9, 127.9, 127.9, 127.6, 127.4, 127.4, 127.3, 127.3, 127.1, 127.1, 121.4, 119.1, 115.3, 81.4, 80.9, 75.16, 75.13, 74.9, 74.4, 73.5, 72.5, 70.3, 69.1, 38.6, 25.4, 21.1; HRMS (EI): *m*/*z* calcd for $C_{43}H_{45}NO_5$ (M^+) 655.3298, found 655.3296.

(1*S*,2*R*,3*S*,4*S*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-7'-chloro-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline] (4w)[S1]



Compound **1b** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **4w** (50.4 mg. 83%): $[\alpha]^{25}_{D}$ +6.5 (*c* 0.81, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.17 (m, 19H), 7.00-6.98 (m, 2H), 6.60 (d, *J* = 8.4 Hz, 1H), 6.49 (brs, 1H), 5.03 (d, *J* = 11.6 Hz, 1H), 4.74 (brs, 2H), 4.63 (d, *J* = 11.6 Hz, 1H), 4.54 (d, *J* = 10.8 Hz, 1H), 4.45-4.37 (m, 3H), 4.15 (d, *J* = 10.8 Hz, 1H), 4.06 (brs, 1H), 3.96 (brs, 1H), 3.84-3.81 (m, 1H), 3.75 (dd, *J* = 2.0 Hz, *J* = 10.0 Hz, 1H), 3.67 (dd, *J* = 8.4 Hz, *J* = 8.8 Hz, 1H), 3.49 (dd, *J* = 5.2 Hz, *J* = 8.8 Hz, 1H), 3.38-3.32 (m, 1H), 3.18-3.12 (m, 1H), 2.41-2.34 (m, 1H), 2.05-2.00 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.1, 139.2, 138.6, 138.4, 137.8, 134.0, 129.5, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.5, 127.4, 127.4, 127.3, 127.3, 127.3, 127.2, 122.4, 117.7, 114.0, 81.4, 80.8, 75.2, 74.9, 74.7, 74.5, 73.5, 72.5, 70.5, 69.0, 38.4, 25.3; HRMS (EI): *m*/*z* calcd for $C_{42}H_{42}ClNO_5$ (M^+) 675.2752, found 675.2758.

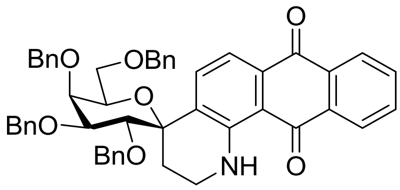
(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-2',2,3',3,4,5-hexahydro-1H-spiro[naphtho[2',3'-h]quinoline-4',1-pyran]-7',12'-dione (4x)



Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the red oil **4x** (42.3 mg. 61%): $[\alpha]^{25}_D$ unable to record (*c* 0.19, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.12 (s, 1H), 8.31-8.29 (m, 1H), 8.25-2.23 (m, 1H), 7.80-7.75 (m, 2H), 7.72-7.68 (m, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.34-7.20 (m, 15H), 7.08-7.06 (m, 3H), 6.93-6.90 (m, 2H), 4.92 (d, *J* = 10.8 Hz, 1H), 4.89 (d, *J* = 9.2 Hz, 2H), 4.63 (d, *J* = 10.8 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 10.8 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.13 (d, *J* = 10.8 Hz, 1H), 4.00-3.97 (m, 1H), 3.91-3.76 (m, 5H), 3.70 (m, 1H), 3.53-3.46 (m, 1H), 2.61-2.55 (m, 1H), 2.10-2.03 (m, 1H); ^{13}C NMR ($CDCl_3$, 100

MHz) δ 184.5, 183.6, 149.6, 138.4, 138.2, 138.0, 137.5, 135.1, 134.0, 133.9, 133.0, 132.8, 132.6, 131.6, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.8, 127.6, 127.6, 127.6, 127.6, 127.6, 127.5, 126.6, 115.3, 112.1, 86.7, 83.2, 78.9, 75.7, 75.6, 75.2, 73.7, 73.4, 72.8, 69.3, 37.3, 25.1; HRMS (EI): *m*/*z* calcd for $C_{50}H_{45}NO_7$ 771.3196, found 771.3198.

(1*S*,2*R*,3*S*,4*S*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-2',3',2,3,4,5-hexahydro-1H-spiro[naphtho[2',3'-h]quinoline-4',1-pyran]-7',12'-dione (4y)



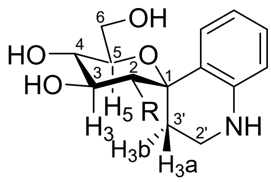
Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the red oil **4y** (48.6 mg. 70%): $[\alpha]^{25}_{D}$ unable to record (*c* 0.26, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.06 (s, 1H), 8.29 (d, *J* = 7.6 Hz, 1H), 8.23 (d, *J* = 6.8 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.76 (dd, *J* = 1.2 Hz, *J* = 6.8 Hz, 1H), 7.69 (dd, *J* = 1.2 Hz, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.39-7.25 (m, 15H), 7.07-7.06 (m, 3H), 6.95-6.92 (m, 2H), 5.05 (d, *J* = 11.6 Hz, 1H), 4.79 (d, *J* = 11.6 Hz, 1H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.66 (d, *J* = 10.4 Hz, 1H), 4.63 (d, *J* = 10.4 Hz, 1H), 4.46 (d, *J* = 11.6 Hz, 1H), 4.41 (d, *J* = 11.6 Hz, 2H), 4.20 (d, *J* = 10.8 Hz, 1H), 4.10 (d, *J* = 2.0 Hz, 1H), 3.90-3.85 (m, 2H), 3.79-3.73 (m, 1H), 3.68 (dd, *J* = 7.6 Hz, *J* = 9.2 Hz, 1H), 3.53 (dd, *J* = 5.6 Hz, *J* = 9.2 Hz, 1H), 3.45-3.42 (m, 1H), 2.53-2.47 (m, 1H), 2.07-2.00 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.5, 183.6, 149.7, 139.0, 138.4, 137.9, 137.8, 135.2, 133.9, 133.8, 133.3, 133.0, 132.7, 132.0, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.2, 128.0, 128.0, 127.9, 127.9, 127.9, 127.9, 127.7, 127.6, 127.5, 127.5, 127.4, 127.3, 127.3, 126.9, 126.6, 115.5, 112.1, 82.0, 80.7, 75.7, 74.8, 74.6, 74.5, 73.5, 72.5, 71.2, 69.0, 37.4, 24.5; HRMS (EI): *m*/*z* calcd for $C_{50}H_{45}NO_7$ 771.3196, found 771.3192.

Typical Procedure for Synthesis of deprotection compounds 5a-5e.

Anomeric spiro-glycosides **4** were dissolved in 5 mL of EtOH/HCl (20/1, v/v), 10% Pd/C (0.03 mmol) was then added to the solution. The mixture was stirred in a hydrogen atmosphere continuously for 2 h. After the reaction was complete, Et_3N was added to neutralize the reaction mixture, and the resulting mixture was filtered and concentrated under vacuum to give a crude mixture, which was then purified by flash column chromatography (DCM/MeOH, 6:1, v/v) to obtain the deprotection compounds **5a-5e** in 78–90% yields.

Spectroscopic Characterization Data of 5a-5e

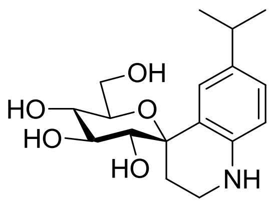
(1*S*,2*R*,3*S*,4*R*,5*R*)-5-(hydroxymethyl)-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline]-2,3,4-triol (5a)



Compound **4a** (0.1 mmol, 64 mg) was treated according to the aforementioned method to give the blue oil **5a** (24.7 mg, 88%): $[\alpha]^{25}_{D}$ unable to record (*c* 0.15, MeOH); ^{1}H NMR (D_2O, 400 MHz) δ 7.37 (1H, d, *J* = 8.0 Hz, H5'), 7.09 (1H, dd, *J* = 7.6 Hz, *J* = 8.0 Hz, H7'), 6.76 (1H, dd, *J* = 7.6 Hz, *J* = 8.0 Hz, H6'), 6.66 (1H, d, *J* = 8.0 Hz, H8'), 3.97 (1H, d, *J* = 10.0 Hz, H2), 3.70-3.56 (2H, m, H3, H6a), 3.62-3.56 (2H, m, H4, H6b), 3.42 (1H, dd, *J* = 9.2 Hz, *J* = 9.2 Hz, H5), 3.17-3.12 (1H, m, H2a'), 3.07-3.01 (1H, m, H2b'), 2.19-2.16 (1H, m, H3a'), 2.03-1.96 (1H, m, H3b'); ^{13}C NMR (D_2O, 100 MHz) δ 146.1, 129.6, 127.0, 122.6, 119.2, 116.8, 75.0 (C-1), 73.8 (C-2), 73.5 (C-3), 72.8 (C-4), 70.5 (C-5), 61.3 (C-6), 36.5 (C-2'), 23.0 (C-3'); HRMS (ESI): *m*/*z* calcd for

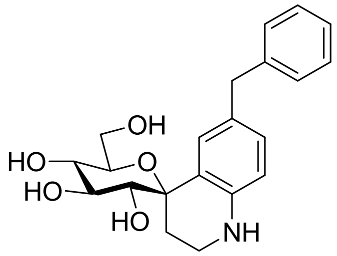
$C_{14}H_{18}NO_5Na$ (M^+) 303.1077, found 303.1078.

(1*S*,2*R*,3*S*,4*R*,5*R*)-5-(hydroxymethyl)-6'-isopropyl-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline]-2,3,4-triol (5b)



Compound **4d** (0.1 mmol, 68 mg) was treated according to the aforementioned method to give the pale yellow oil **5b** (29.0 mg, 90%): $[\alpha]^{25}_D$ +2.2 (*c* 0.22, MeOH); ^{1}H NMR (D_2O, 400 MHz) δ 7.25 (s, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.64 (dd, *J* = 8.4 Hz, 1H), 4.00 (d, *J* = 9.6 Hz, 1H), 3.72-3.59 (m, 4H), 3.42 (dd, *J* = 9.2 Hz, *J* = 9.2 Hz, 1H), 3.14-3.11 (m, 1H), 3.02 (dd, *J* = 11.2 Hz, *J* = 11.6 Hz, 1H), 2.77-2.70 (m, 1H), 2.17 (d, *J* = 14.0 Hz, 1H), 2.00 (dd, *J* = 11.2 Hz, *J* = 14.0 Hz, 1H), 1.08 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (D_2O, 100 MHz) δ 144.1, 140.4, 127.5, 124.7, 122.8, 117.1, 75.2, 74.0, 73.6, 72.8, 70.7, 61.5, 36.8, 33.0, 23.4, 23.3, 23.3; HRMS (ESI): *m*/*z* calcd for $C_{17}H_{25}NO_5Na$ (M^+) 345.1547, found 345.1552.

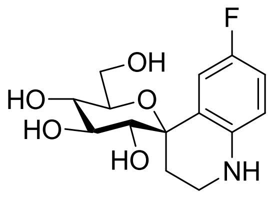
(1*S*,2*R*,3*S*,4*R*,5*R*)-6'-benzyl-5-(hydroxymethyl)-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline]-2,3,4-triol (5c)



Compound **4d** (0.1 mmol, 68 mg) was treated according to the aforementioned method to give the pale yellow oil **5c** (27.3 mg, 82%): $[\alpha]^{25}_D$ +2.2 (*c* 0.07, MeOH); ^{1}H NMR

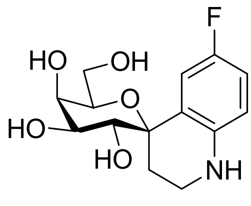
(D_2O, 400 MHz) 7.25-7.12 (m, 6H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.60 (d, *J* = 8.4 Hz, 1H), 3.91 (d, *J* = 9.6 Hz, 1H), 3.80 (s, 2H), 3.70-3.64 (m, 2H), 3.59-3.56 (m, 2H), 3.39 (dd, *J* = 9.2 Hz, *J* = 9.2 Hz, 1H), 3.13-3.09 (m, 1H), 3.01 (dd, *J* = 11.2 Hz, *J* = 11.6 Hz, 1H), 2.17-2.12 (m, 1H), 2.02-1.95 (m, 1H); ^{13}C NMR (D_2O, 100 MHz) δ 144.5 (unable to record), 142.3, 132.3, 130.0, 128.7, 128.7, 128.7, 128.7, 127.0, 126.1, 122.8, 117.2, 75.1, 74.0, 73.6, 72.8, 70.6, 61.3, 40.4, 36.7, 23.2; HRMS (EI): *m*/*z* calcd for $C_{21}H_{24}NO_5Na$ (M+) 393.1547, found 393.1554.

(1*S*,2*R*,3*S*,4*R*,5*R*)-6'-fluoro-5-(hydroxymethyl)-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline]-2,3,4-triol (5d)



Compound **4g** (0.08 mmol, 52.7 mg) was treated according to the aforementioned method to give the pale yellow oil **5d** (18.7 mg, 78%): $[\alpha]^{25}_D$ +8.6 (*c* 0.15, MeOH); ^1H NMR (D_2O, 400 MHz) δ 7.15 (d, *J* = 10.6 Hz, 1H), 6.87 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 6.65 (dd, *J* = 6.8 Hz, *J* = 7.2 Hz, 1H), 3.86 (d, *J* = 9.6 Hz, 1H), 3.71-3.59 (m, 4H), 3.43 (dd, *J* = 8.4 Hz, *J* = 9.2 Hz, 1H), 3.15-3.12 (m, 1H), 3.01 (dd, *J* = 11.2 Hz, *J* = 11.6 Hz, 1H), 2.16 (d, *J* = 13.6 Hz, 1H), 2.01 (dd, *J* = 12.0 Hz, *J* = 13.6 Hz, 1H); ^{13}C NMR (D_2O, 100 MHz) δ 156.4 (d, *J* = 232.7 Hz), 142.6, 123.9, 118.2 (d, *J* = 7.9 Hz), 116.6 (d, *J* = 23.1 Hz), 113.0 (d, *J* = 22.8 Hz), 75.0, 74.3, 73.4, 72.9, 70.4, 61.2, 36.9, 23.1; HRMS (ESI): *m*/*z* calcd for $C_{14}H_{18}FNO_5Na$ (M^+) 321.0983, found 321.0986.

(1*S*,2*R*,3*S*,4*S*,5*R*)-6'-fluoro-5-(hydroxymethyl)-2',2,3',3,4,5-hexahydro-1'H-spiro[pyran-1,4'-quinoline]-2,3,4-triol (5e)



Compound **4r** (0.08 mmol, 52.7 mg) was treated according to the aforementioned method to give the pale yellow oil **5e** (22.5 mg, 94%): $[\alpha]^{25}_{D}$ +8.6 (*c* 0.13, MeOH); ^{1}H NMR (D_2O, 400 MHz) δ 7.20 (dd, *J* = 2.8 Hz, *J* = 10.8 Hz, 1H), 6.90-6.85 (m, 1H), 6.65 (dd, *J* = 5.2 Hz, *J* = 9.2 Hz, 1H), 4.20 (d, *J* = 10.4 Hz, 1H), 3.95 (d, *J* = 2.8 Hz, 1H), 3.88-3.82 (m, 2H), 3.64-3.54 (m, 2H), 3.16-3.11 (m, 1H), 3.05-2.98 (m, 1H), 2.21-2.16 (m, 1H), 2.03-1.95 (m, 1H); ^{13}C NMR (D_2O, 100 MHz) δ 156.4 (d, *J* = 232.4 Hz), 142.5, 124.1, 118.1 (d, *J* = 7.5 Hz), 116.5 (d, *J* = 22.7 Hz), 113.2 (d, *J* = 23.1 Hz), 75.5, 71.8, 71.0, 70.1, 69.4, 61.2, 37.0, 22.4; HRMS (ESI): *m/z* calcd for $C_{14}H_{18}FNO_5Na$ (M^+) 321.0983, found 321.0988.

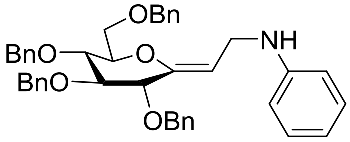
Typical Procedure for Synthesis of side products 3a-I, 3a-II

To a solution of *exo*-glucal **1a** (0.09 mmol), arylamines **2a** (0.11 mmol) and acetic acid (0.45 mmol) in dichloroethane (DCE) (2.0 mL) was added $ZnCl_2$ (0.14 mmol). The reaction mixture was stirred at 65 °C under N_2 for 8 h. After the reaction was complete, CH_2Cl_2 (50 mL) was added to the reaction mixture, washed twice with H_2O (20 mL for each), twice with brine (20 mL for each), and dried over $MgSO_4$. The collected organic layer was concentrated under reduced pressure. Finally, the reaction mixture was purified by silica gel column chromatography with *n*-hexane/ethyl acetate (3/1) to give products **3a-I**, **3a-II** in 8% and 24% yields.

Spectroscopic Characterization Data of 3a-I, 3a-II

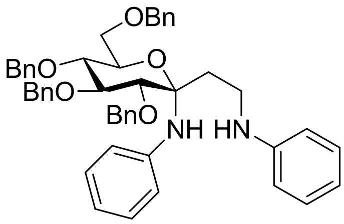
***N*-((Z)-2-((2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)tetrahydro-**

2H-pyran-2-ylidene)ethyl)aniline (3a-I)[S1]



Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the yellow oil **3a-I** (4.6 mg, 8%): $[\alpha]^{25}{}_{D}$ +44.0 (*c* 0.10, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34-7.25 (*m*, 18 H), 7.18-7.14 (m, 4H), 6.70 (m, 1H), 6.63 (m, 2H), 5.10 (m, 1H), 4.78 (d, *J* = 8.4 Hz, 1H), 4.76 (d, *J* = 8.4 Hz, 1H), 4.68 (d, *J* = 6.4 Hz, 1H), 4.66 (d, *J* = 6.4 Hz, 1H), 4.63 (d, *J* = 11.6 Hz, 1H), 4.57 (d, *J* = 11.6 Hz, 1H), 4.55 (d, *J* = 9.6 Hz, 1H), 4.52 (d, *J* = 9.6 Hz, 1H), 3.94-3.69 (m, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.1, 148.2, 138.1, 138.1, 138.0, 137.7, 129.1, 129.1, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 127.9, 127.9, 127.8, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7, 127.7, 127.6, 117.4, 113.2, 113.1, 107.6, 84.6, 78.6, 77.7, 77.5, 74.2, 77.2, 73.9, 73.5, 72.3, 68.7, 38.7; HRMS (EI): *m*/*z* (M^+) calcd for $C_{42}H_{43}NO_5$ 641.3141; found 641.3148.

(1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-tris(benzyloxy)-5-((benzyloxy)methyl)-*N*-phenyl-2-(2-(phenylamino)ethyl)tetrahydro-2H-pyran-1-amine (3a-II) [S1]



Compound **1a** (0.09 mmol, 51 mg) was treated according to the aforementioned method to give the brown oil **3a-II** (15.9 mg, 24%):$[\alpha]^{25}{}_{D}$ +44.0 (*c* 0.15, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.39-7.24 (*m*, 18 H), 7.18-7.16 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.92-6.90 (m, 2H), 6.76 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 6.62 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 6.44-6.42 (m, 2H), 4.96 (d, J = 11.0 Hz, 1H), 4.94 (d, J = 11.0 Hz, 1H), 4.86 (d, J = 11.0 Hz, 1H), 4.81 (d, J = 11.0 Hz, 1H), 4.71 (d, J = 11.0 Hz, 1H), 4.69 (d, J = 11.0 Hz, 1H), 4.59 (d, J = 11.0 Hz, 1H), 4.55 (d, J = 11.0 Hz, 1H), 4.42 (brs, 1H), 4.08 (dd, J= 9.0 Hz, J= 9.0 Hz, 1H), 4.02-3.99 (m, 1H), 3.82 (dd, J= 3.5 Hz, J= 11.0 Hz, 1H), 3.78-3.72 (m, 2H), 3.69 (d, J = 9.0 Hz, 1H), 3.06-3.04 (m, 2H), 2.54-2.48 (m, 1H), 1.87-1.82 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 148.4, 144.3, 138.4, 138.2, 138.0, 137.7, 129.0, 129.0, 129.0, 129.0, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.0, 128.0, 128.0, 127.7, 127.7, 127.6, 127.6, 127.6, 127.6, 127.5, 127.5, 127.5, 119.1, 116.9, 116.6, 116.6, 112.9, 112.9, 89.6, 84.3, 79.4, 78.5, 75.6, 75.2, 74.7, 73.4, 70.6, 68.9, 39.5, 32.1; HRMS (EI): *m*/*z* (M^+) calcd for $C_{48}H_{50}N_2O_5$ 734.3720; found 734.3730.

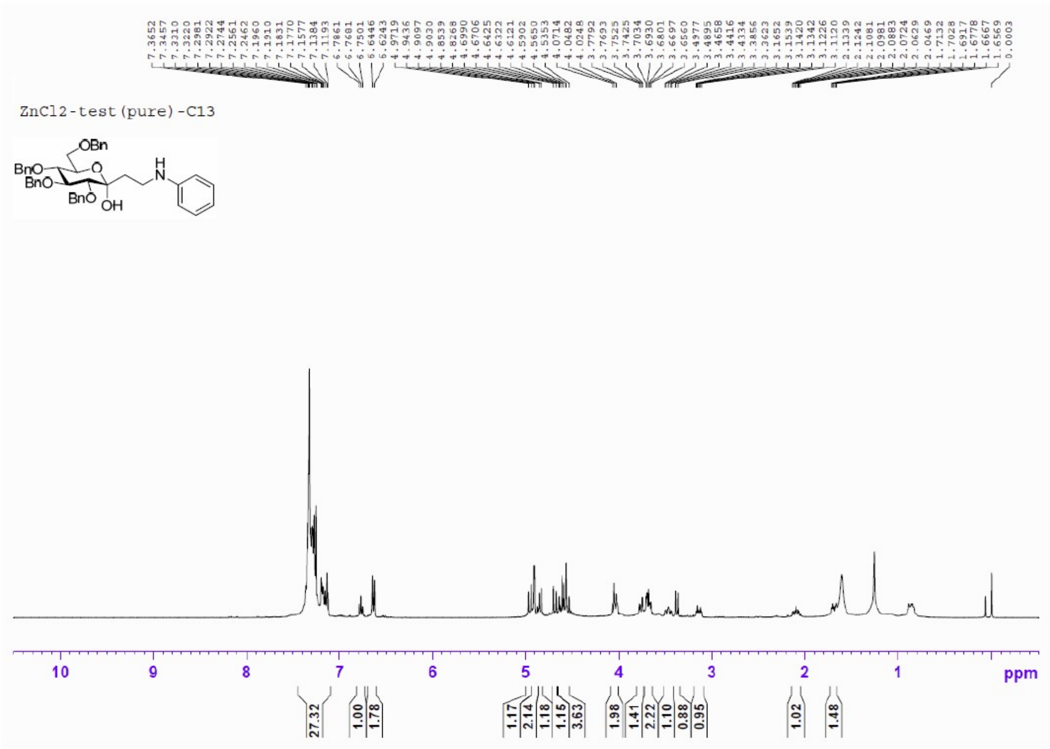
Reference:

S1. P.-Y. Chen, Y.-T. Chiang, M.-T. Hsieh, Y.-C. Hseu, C.-H. Lin,* H.-C. Lin.* Expeditious and Stereoselective Synthesis of (1*S*)-Spiro- [pyran-4-quinolines]. *Eur. J. Org. Chem.* **2022**, e202201116.

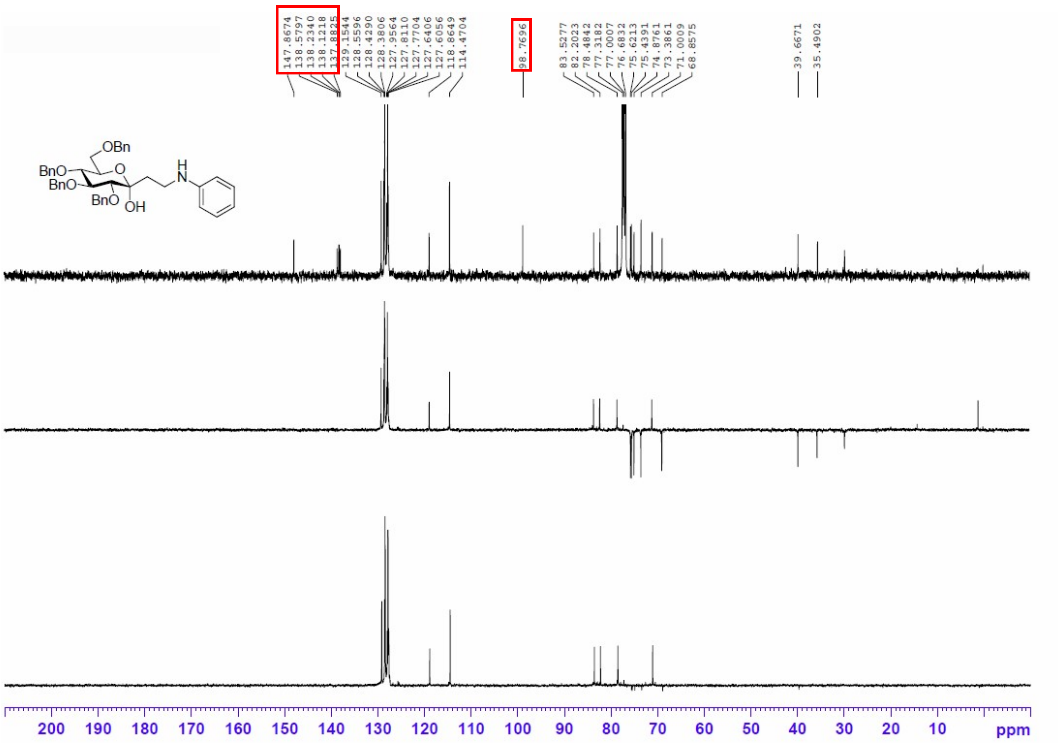
NMR Spectra

¹H and ¹³C NMR spectra of 3a-3r

¹H NMR spectrum of **3a**

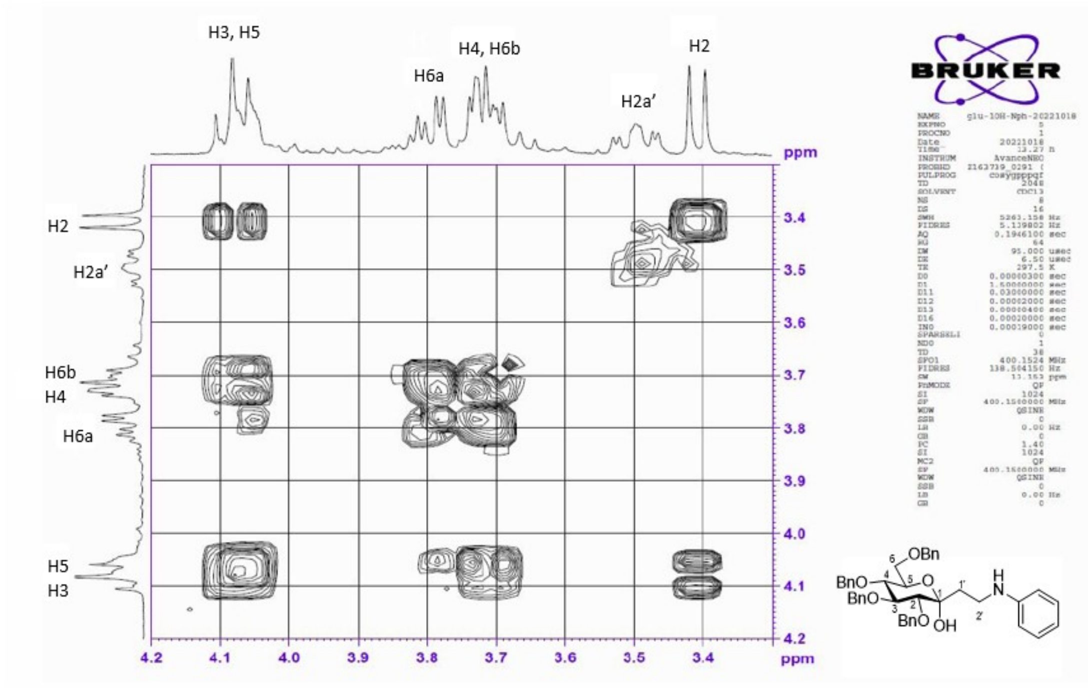


¹³C NMR spectra of **3a**

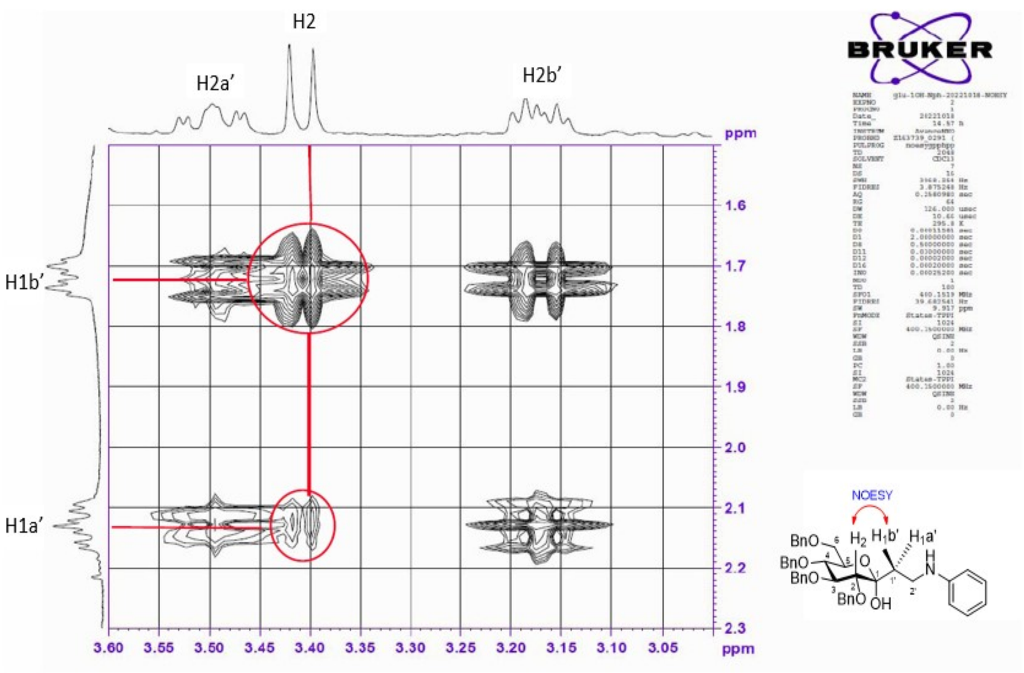


2D NMR Spectra of 3a

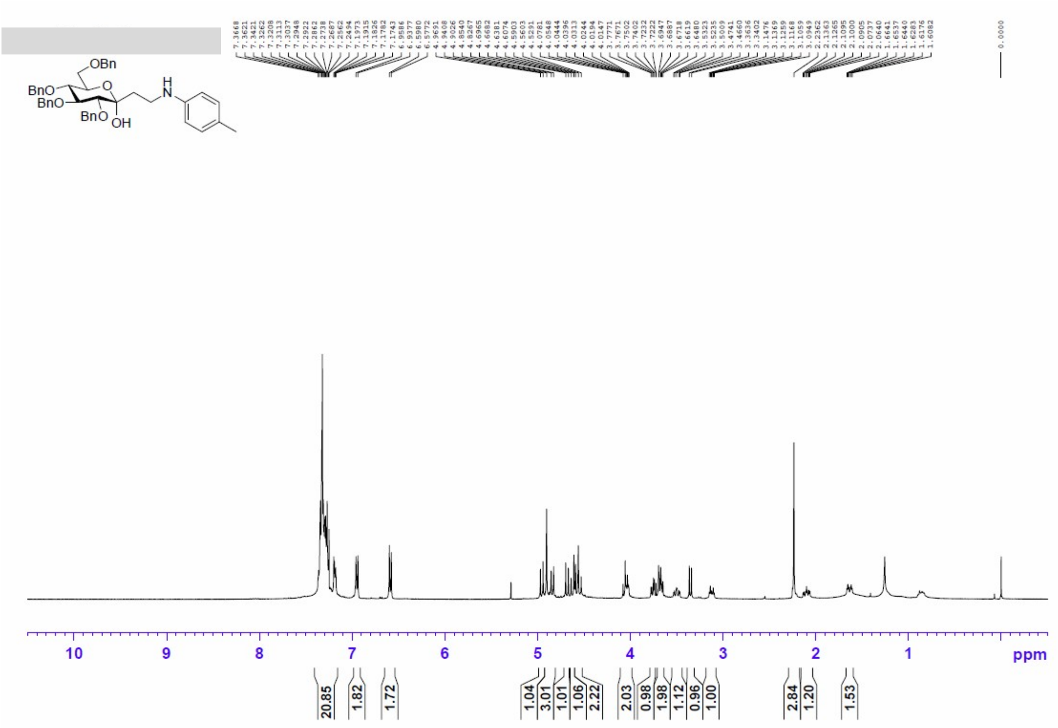
H-H COSY NMR spectrum of **3a**



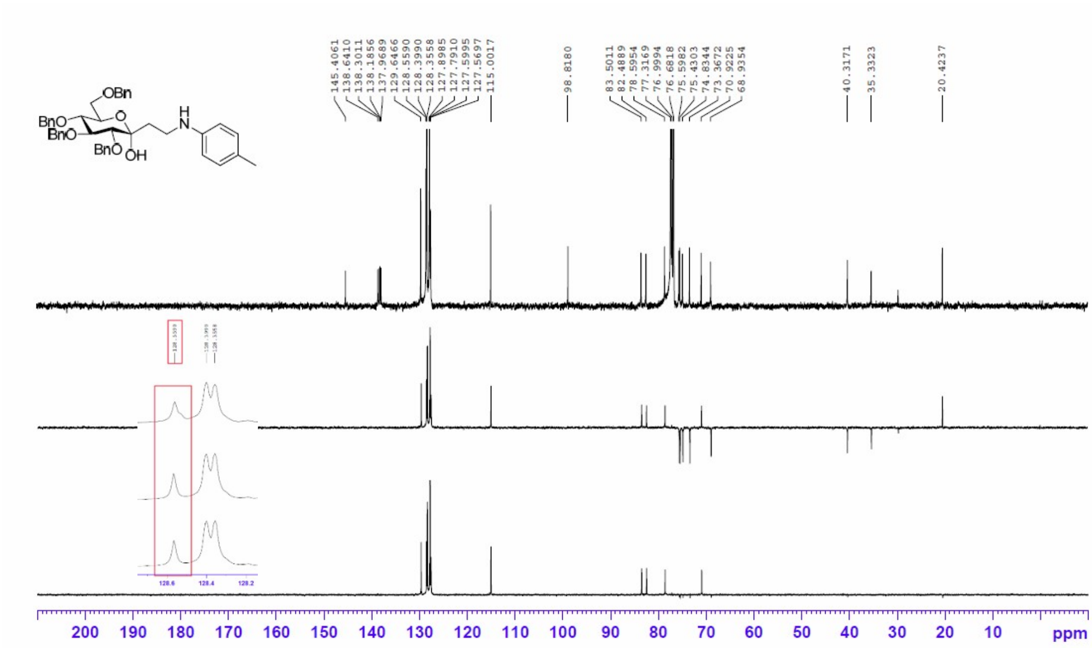
NOESY NMR spectrum of **3a**



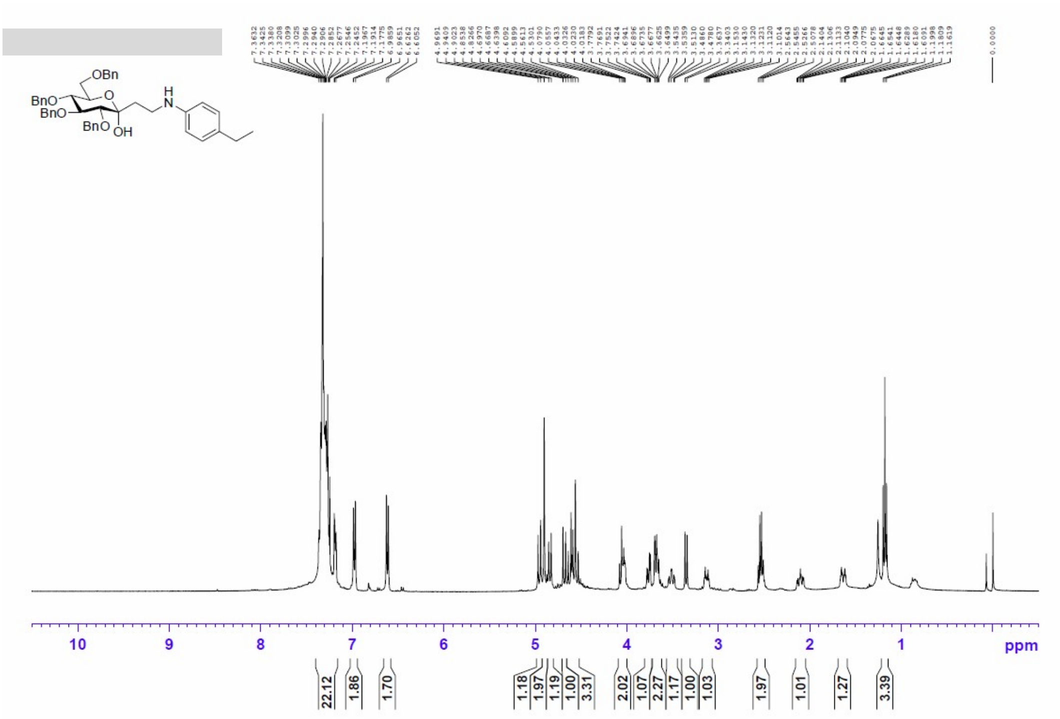
^{1}H NMR spectrum of **3b**



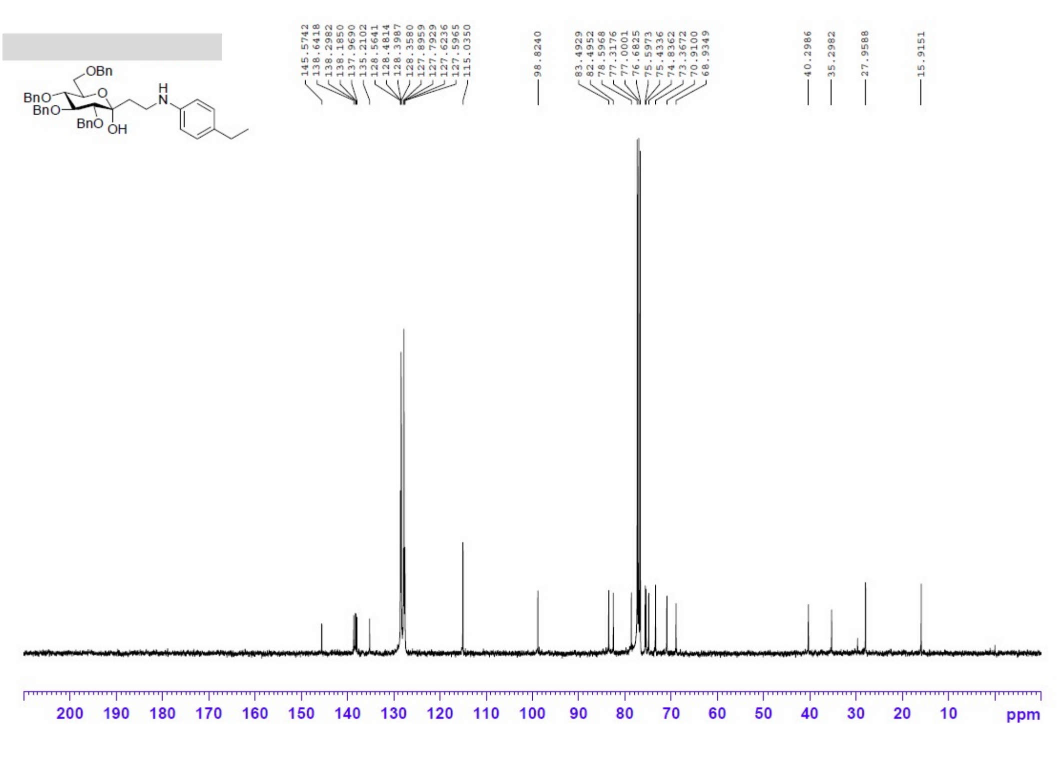
^{13}C NMR spectra of **3b**



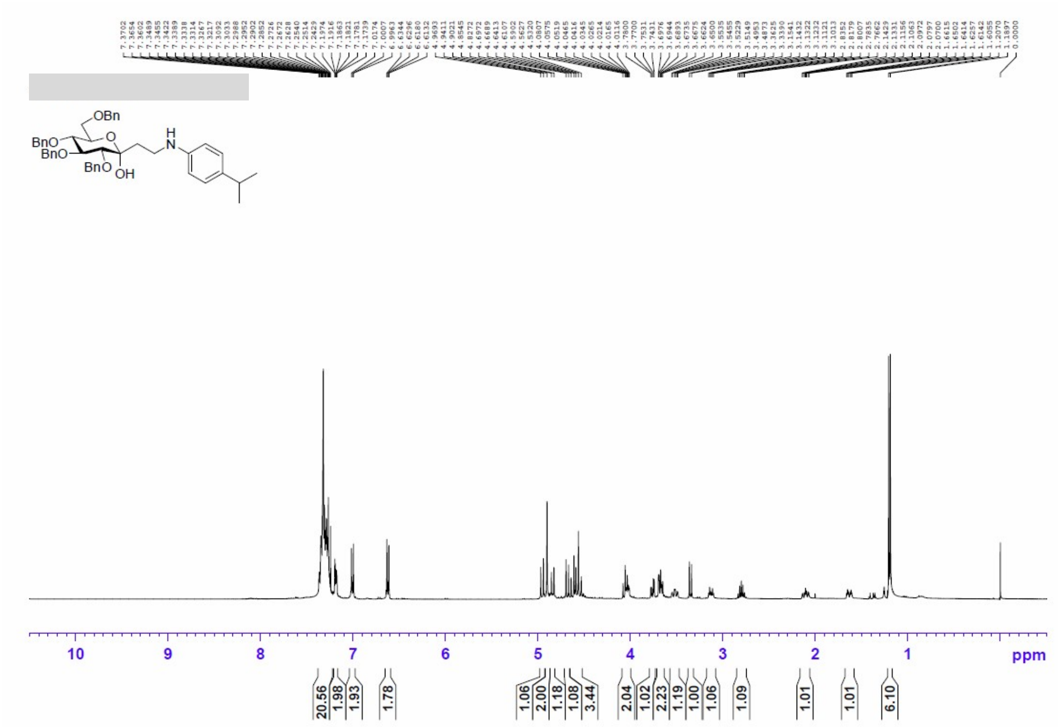
^{1}H NMR spectrum of **3c**



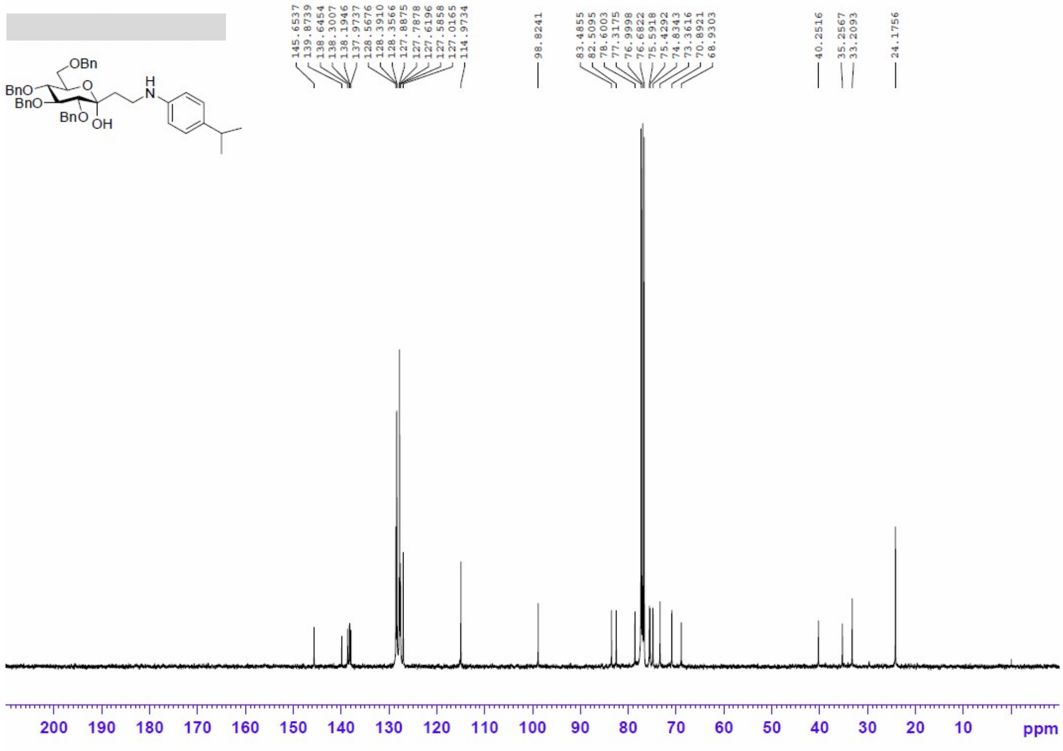
^{13}C NMR spectra of **3c**



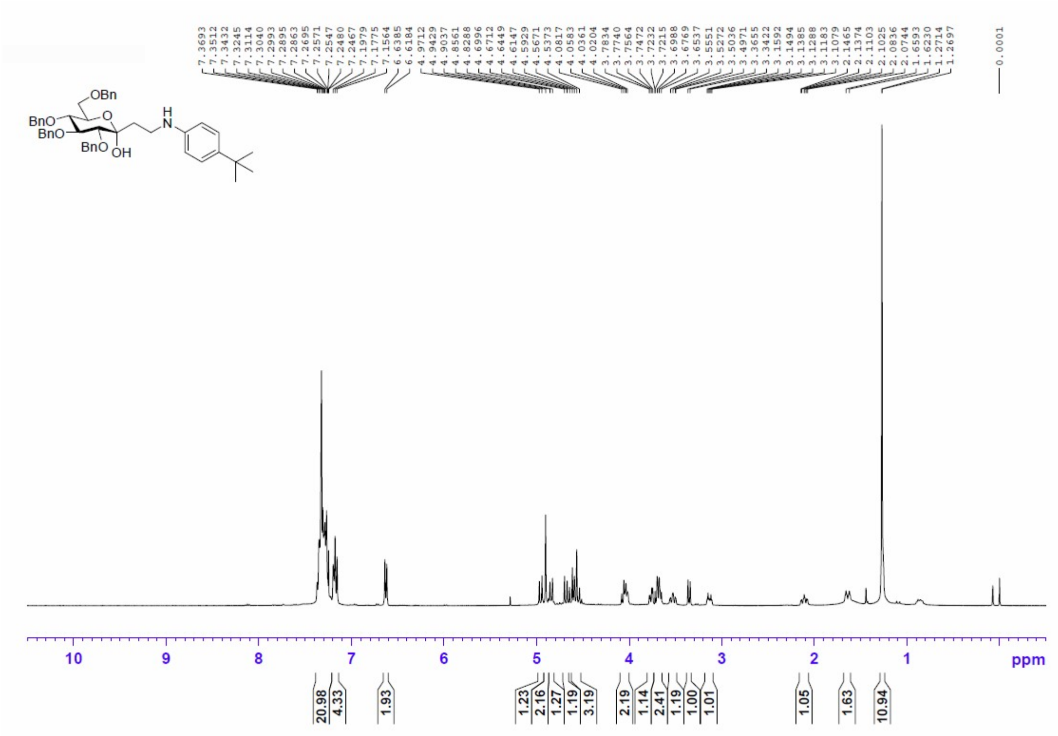
[1]H NMR spectrum of **3d**



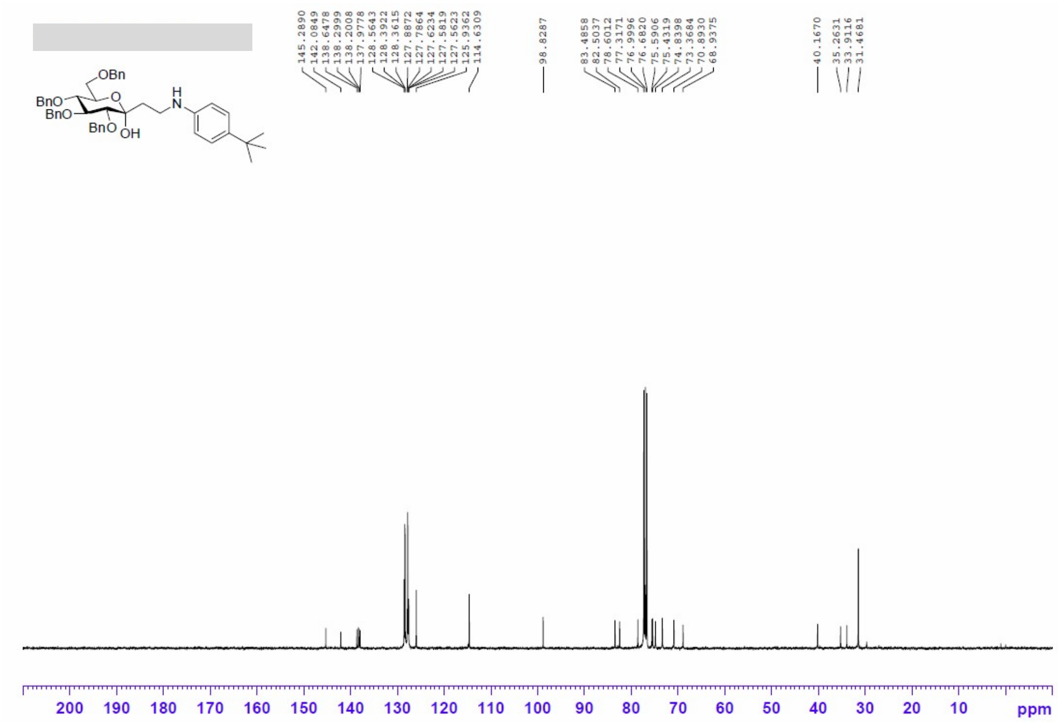
[13]C NMR spectra of **3d**



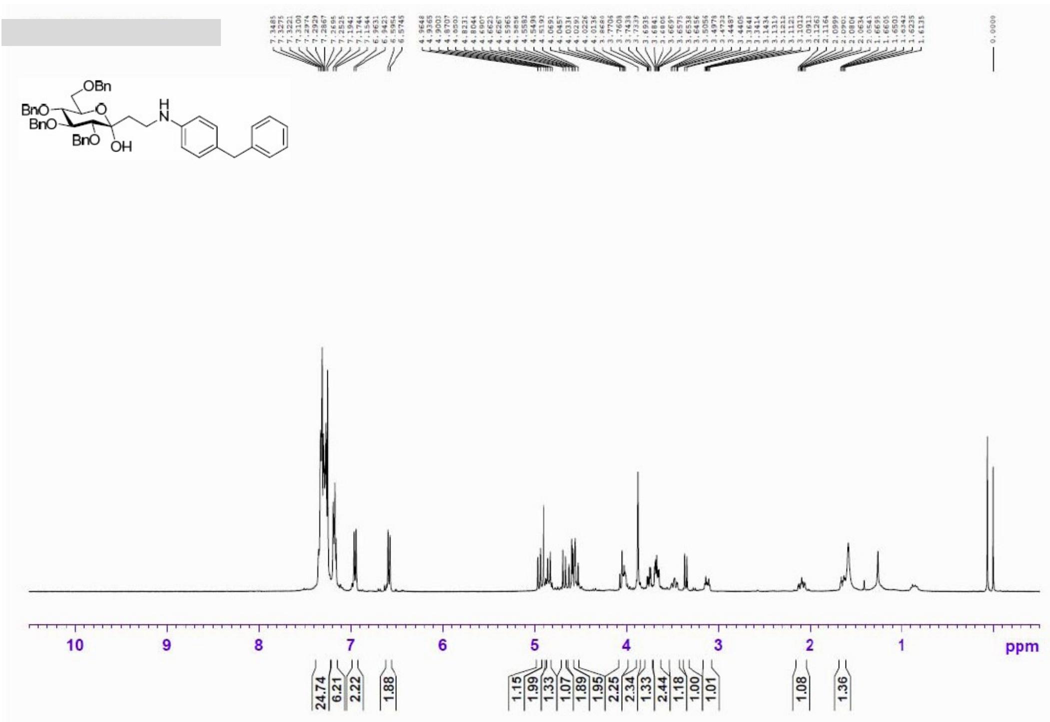
^{1}H NMR spectrum of **3e**



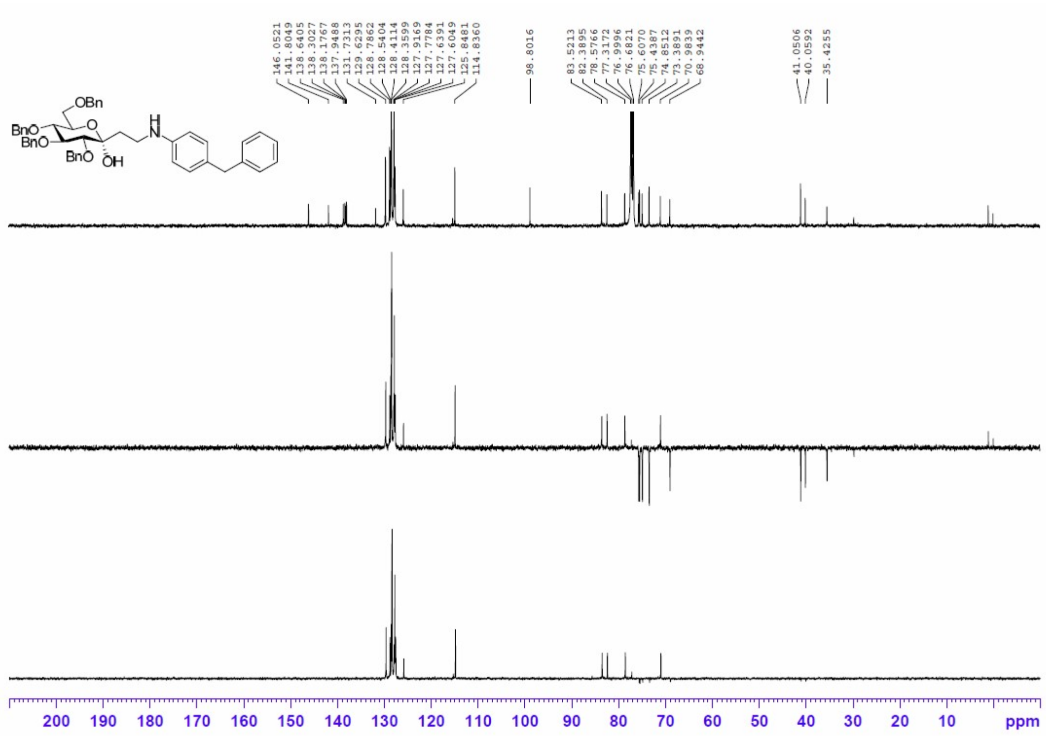
^{13}C NMR spectra of **3e**



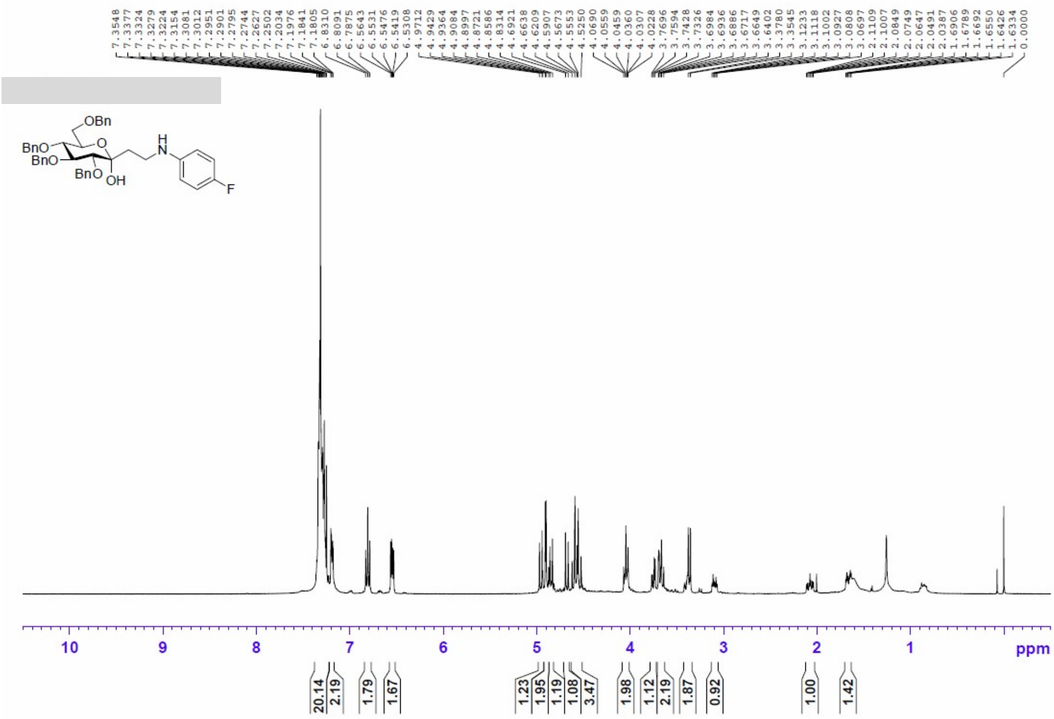
[1]H NMR spectrum of **3f**



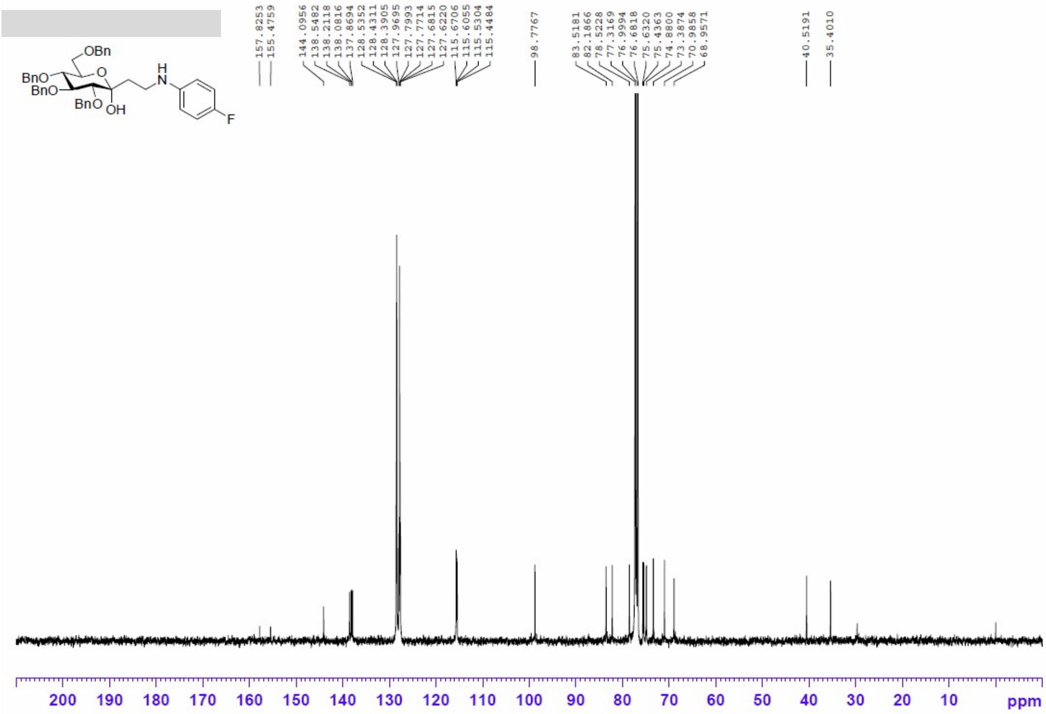
[13]C NMR spectra of **3f**



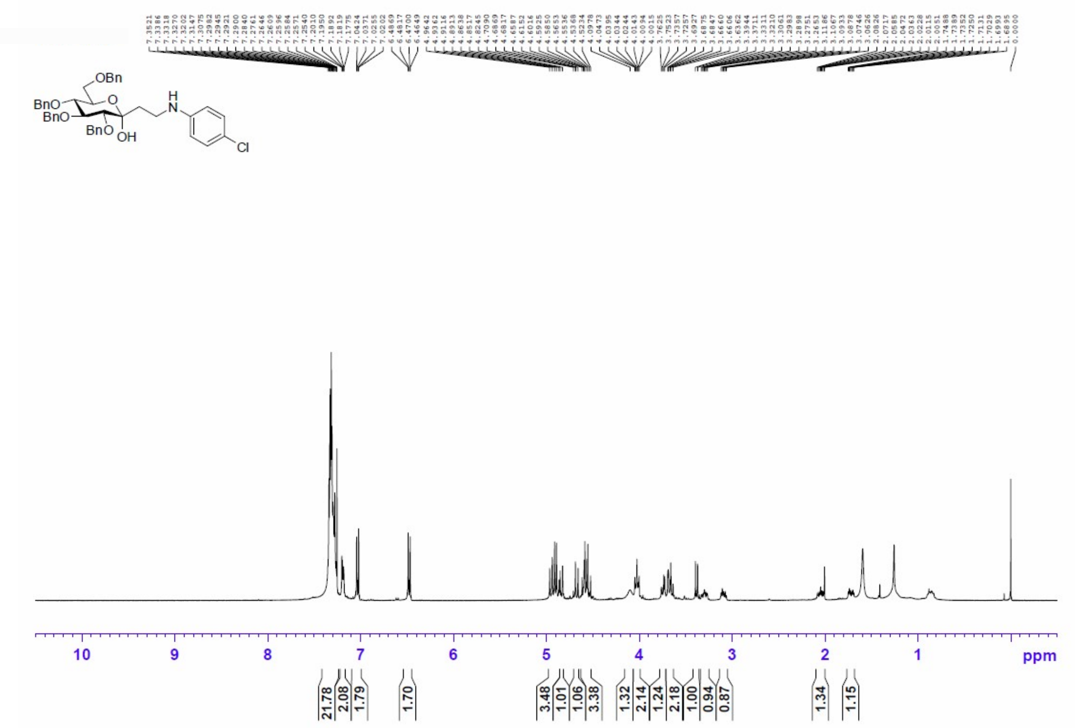
^{1}H NMR spectrum of **3g**



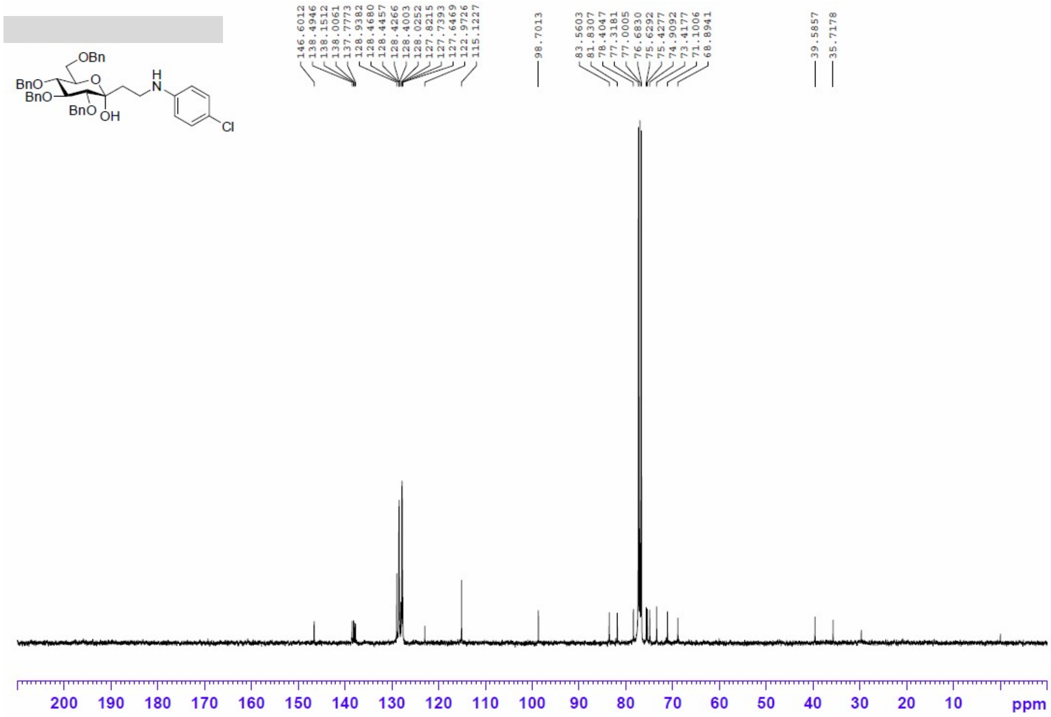
^{13}C NMR spectra of **3g**



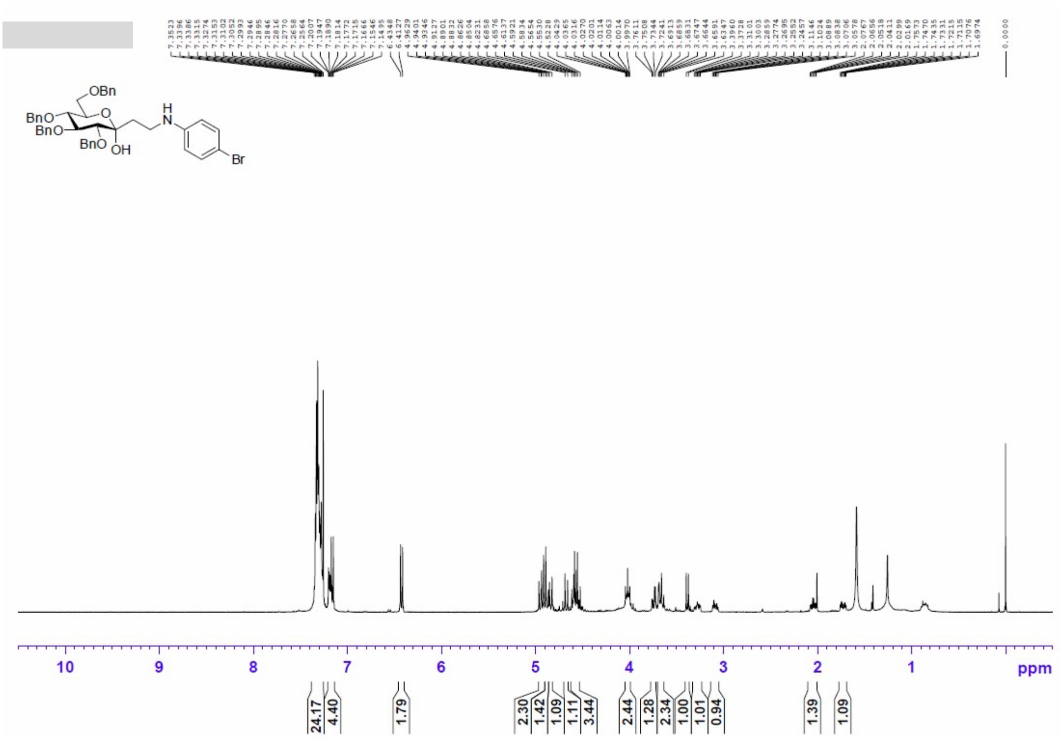
^{1}H NMR spectrum of **3h**



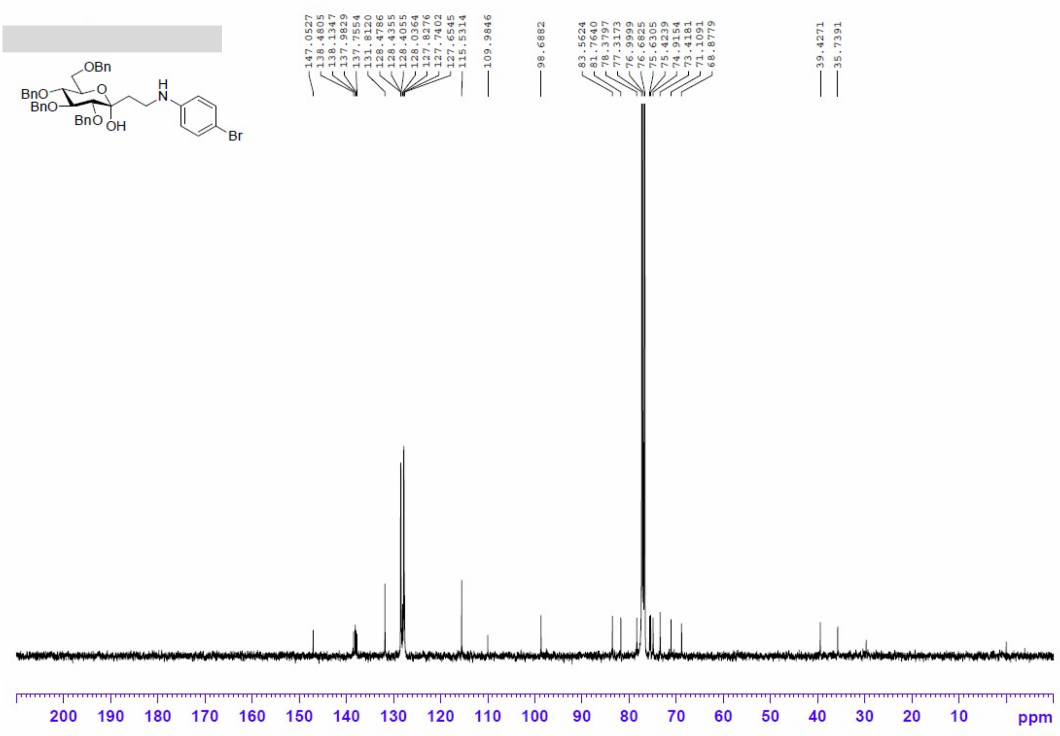
^{13}C NMR spectra of **3h**



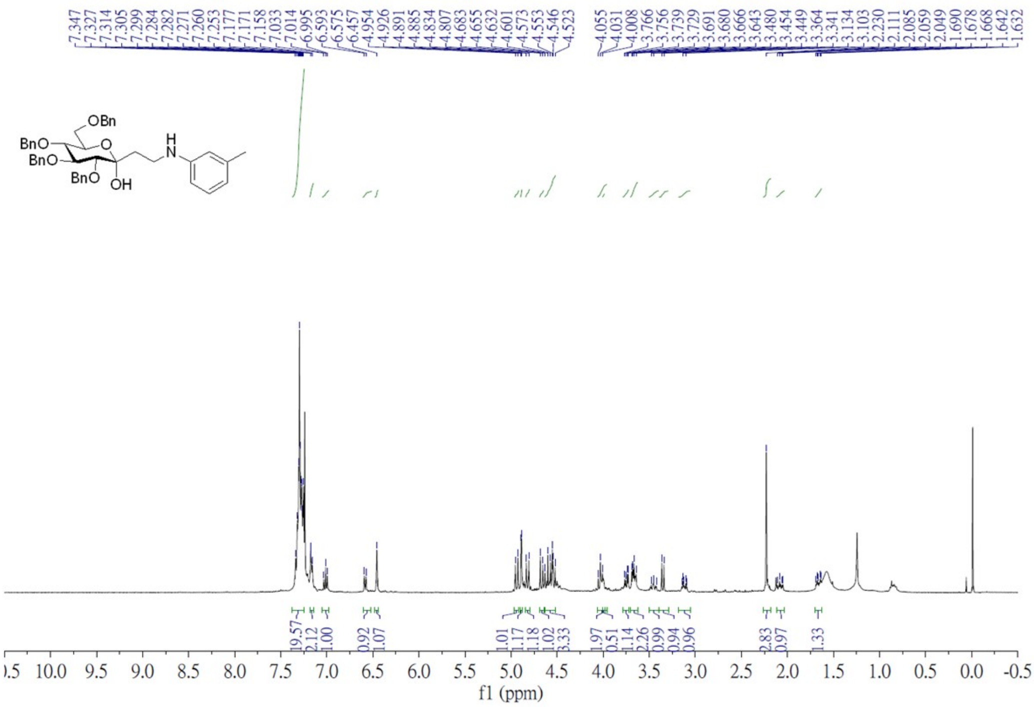
[1]H NMR spectrum of **3i**



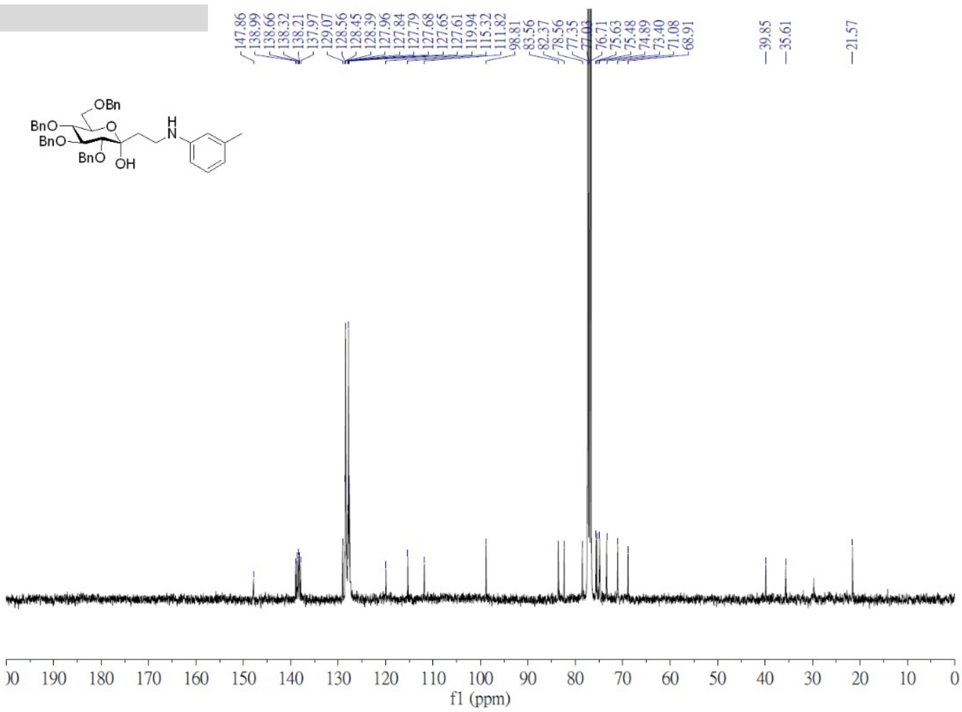
[13]C NMR spectra of **3i**



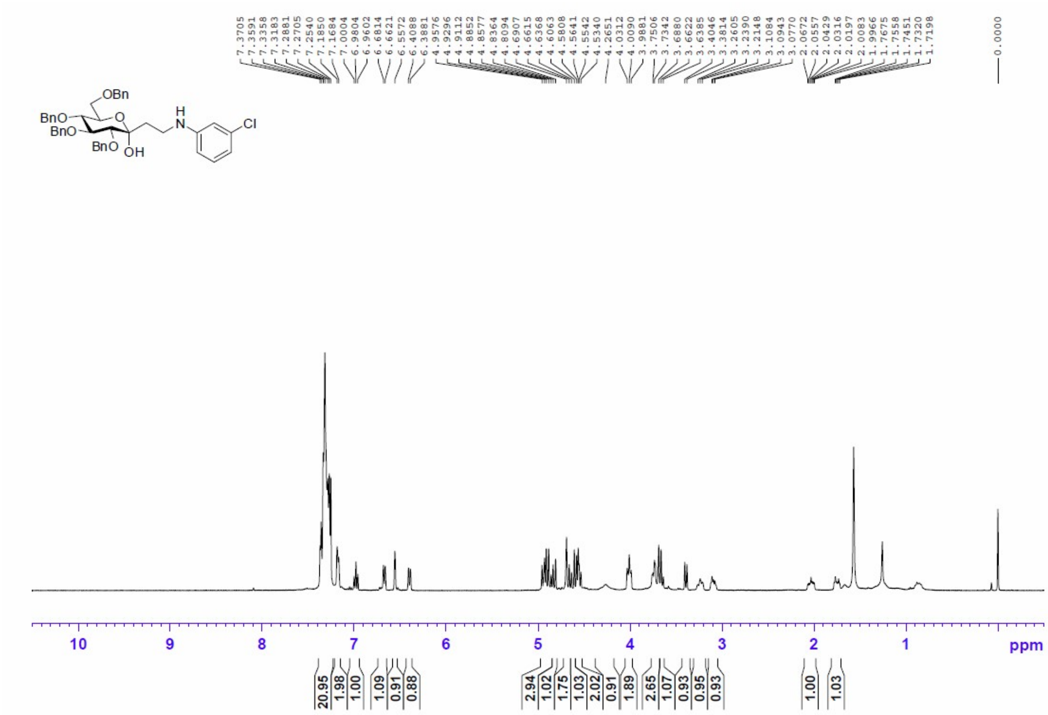
^{1}H NMR spectrum of **3j**



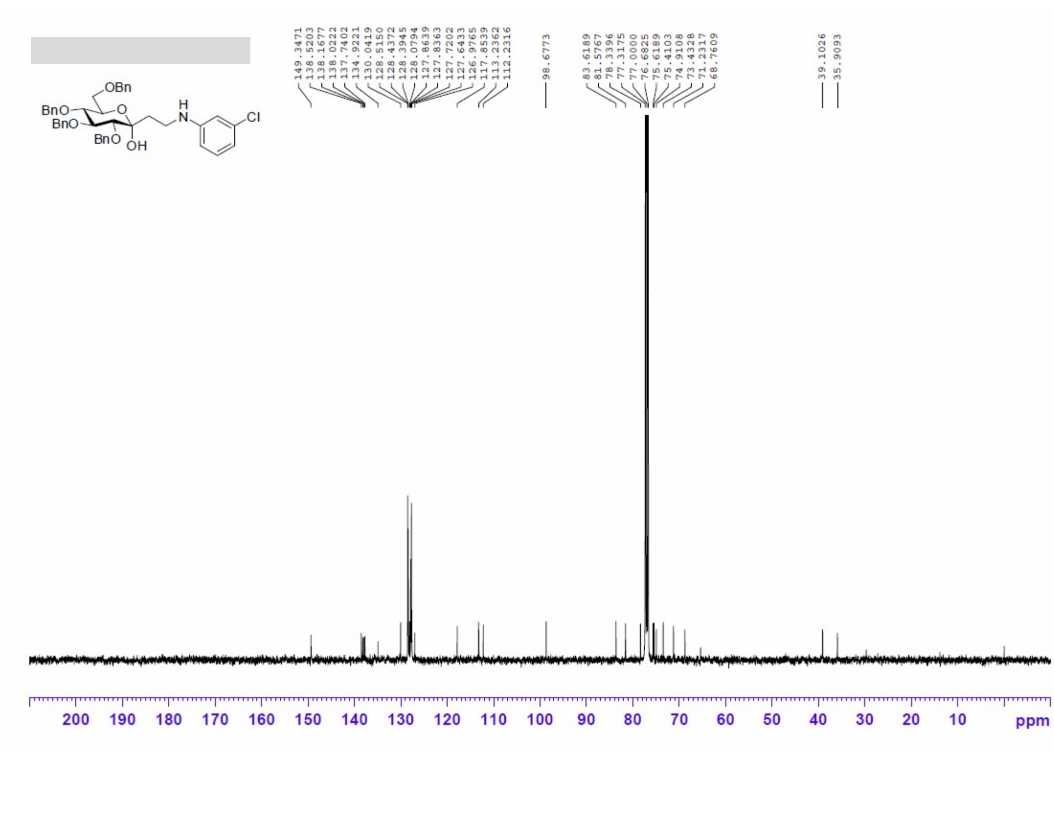
^{13}C NMR spectra of **3j**



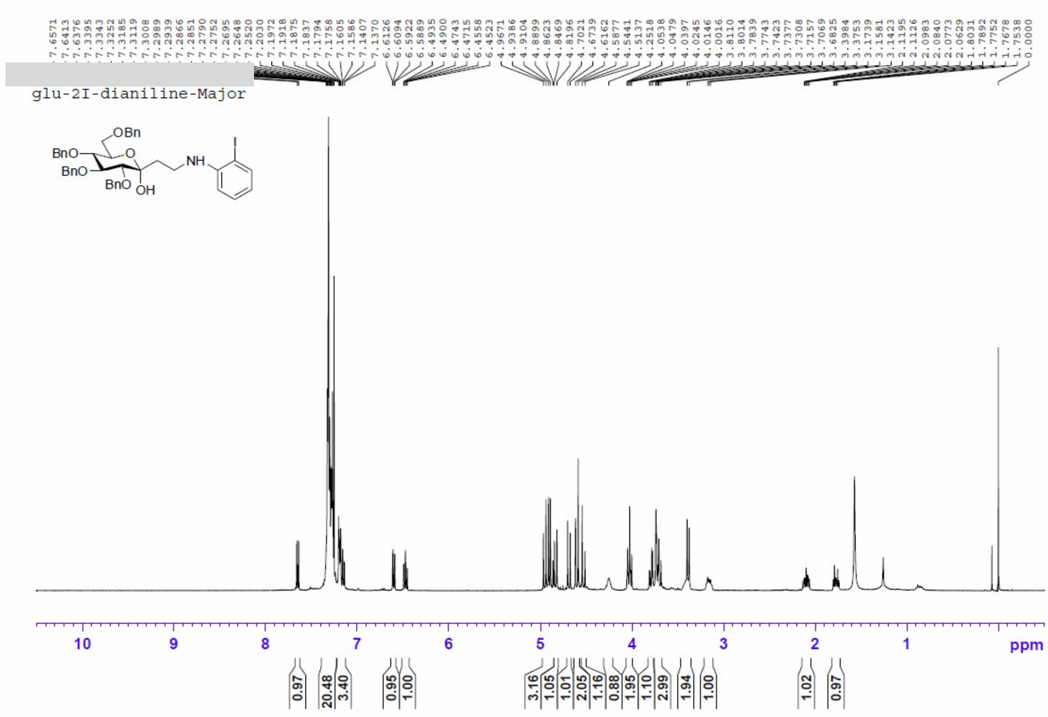
^{1}H NMR spectrum of **3k**



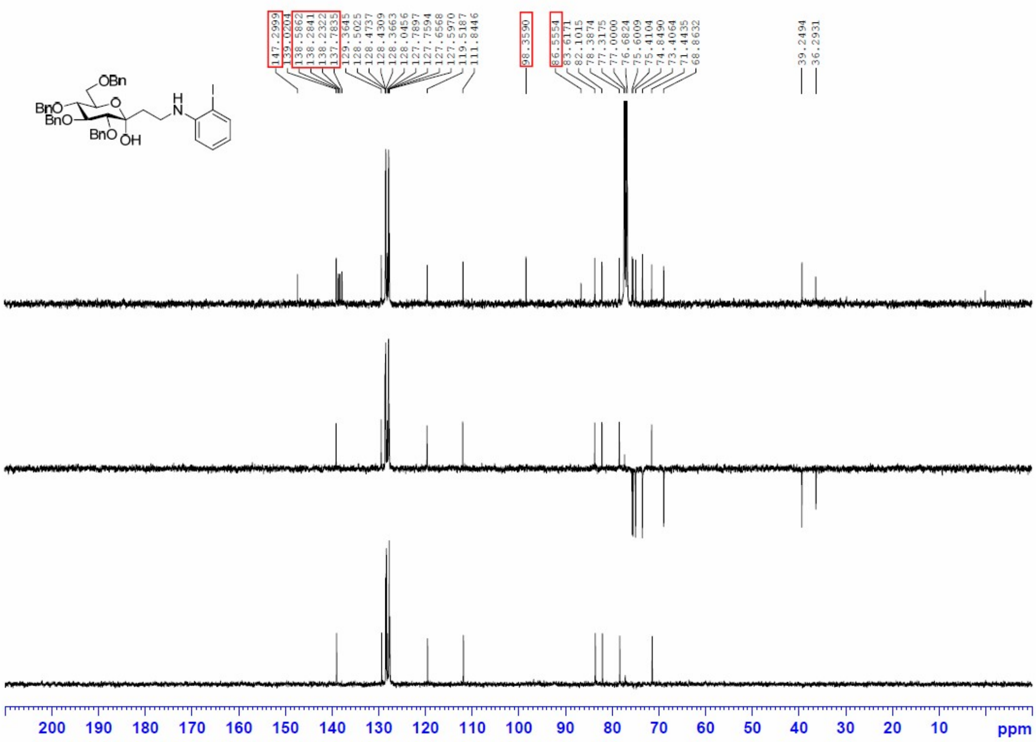
^{13}C NMR spectra of **3k**



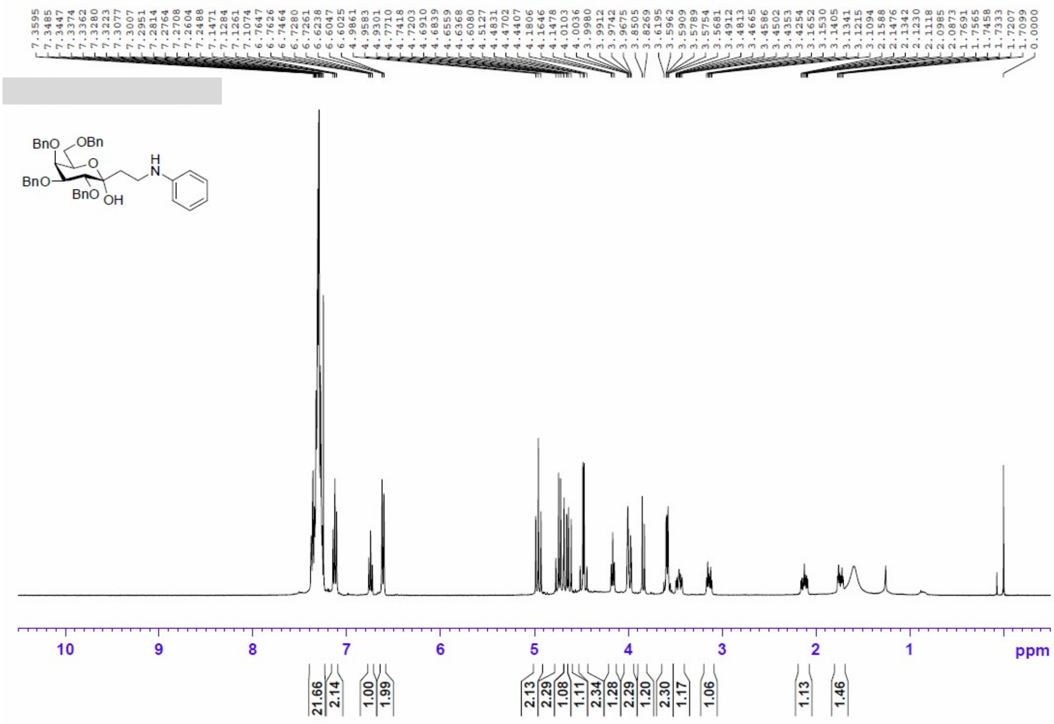
^{1}H NMR spectrum of **3l**



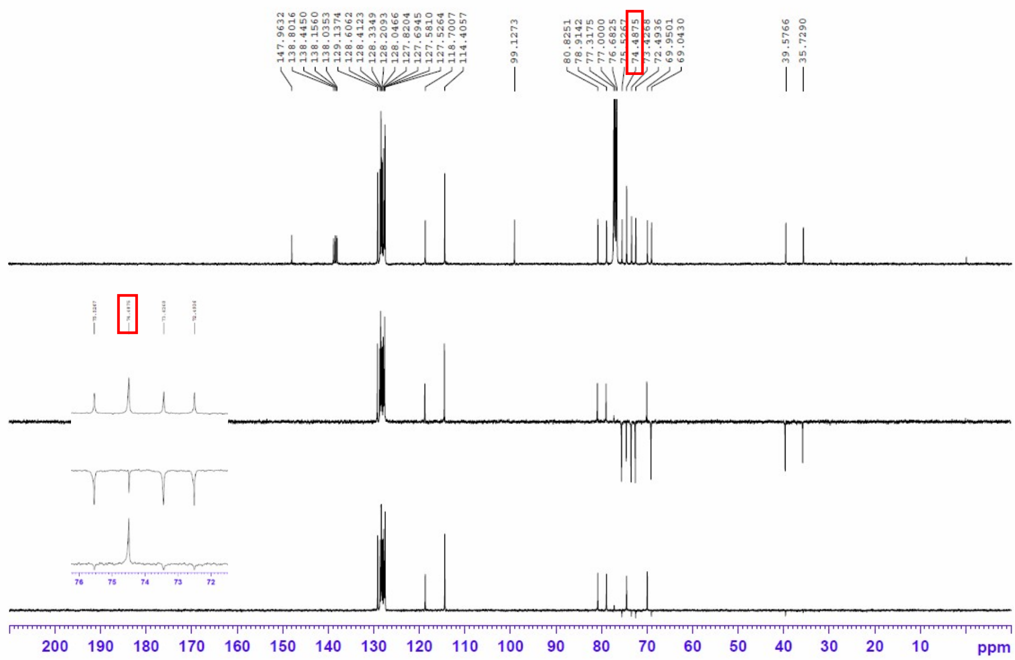
^{13}C NMR spectra of **3l**



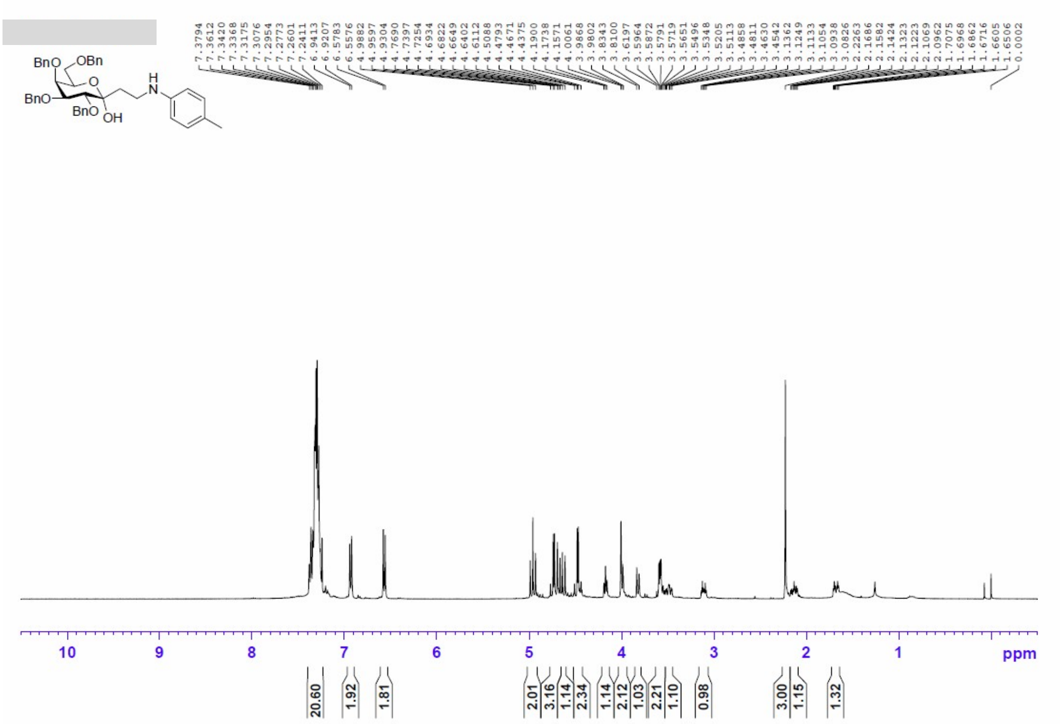
[1]H NMR spectrum of **3m**



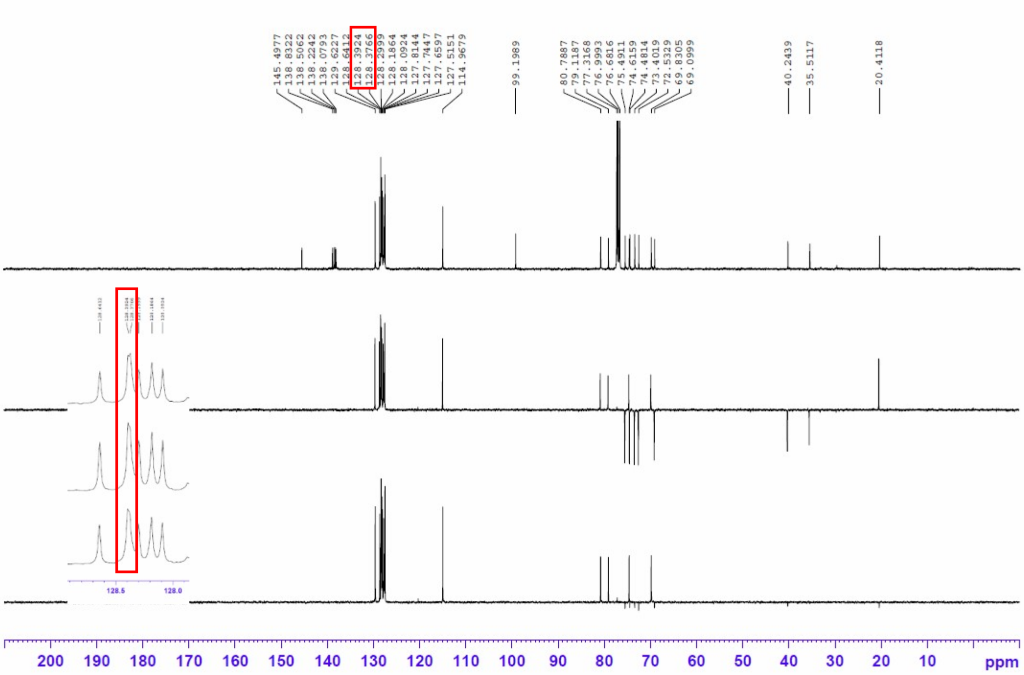
[13]C NMR spectra of **3m**



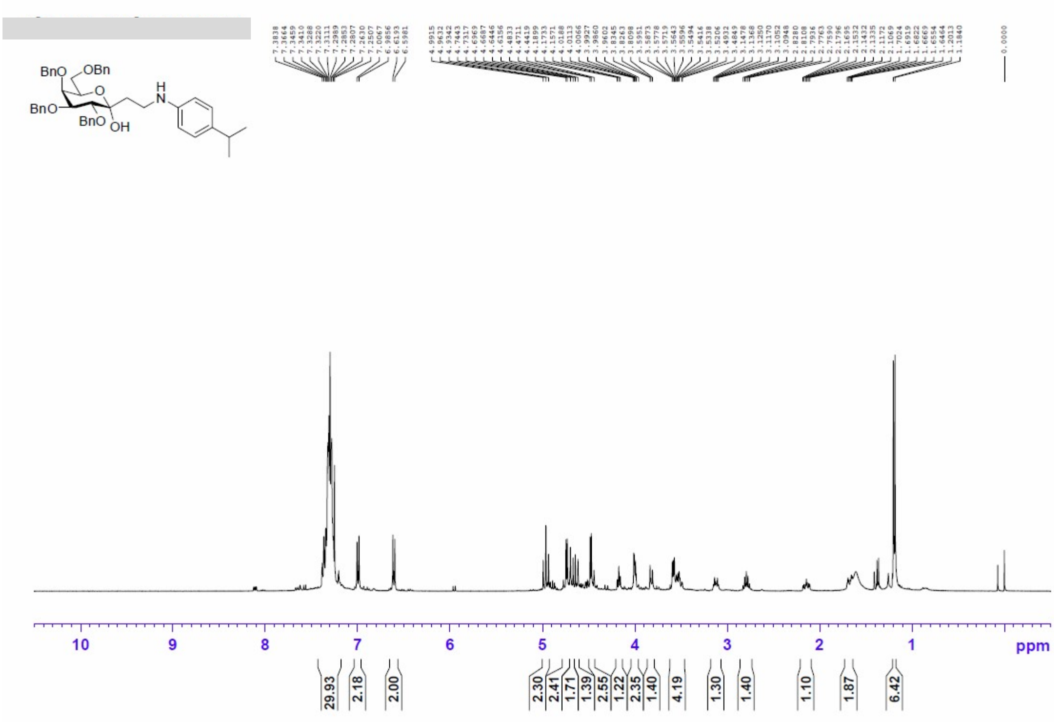
^{1}H NMR spectrum of **3n**



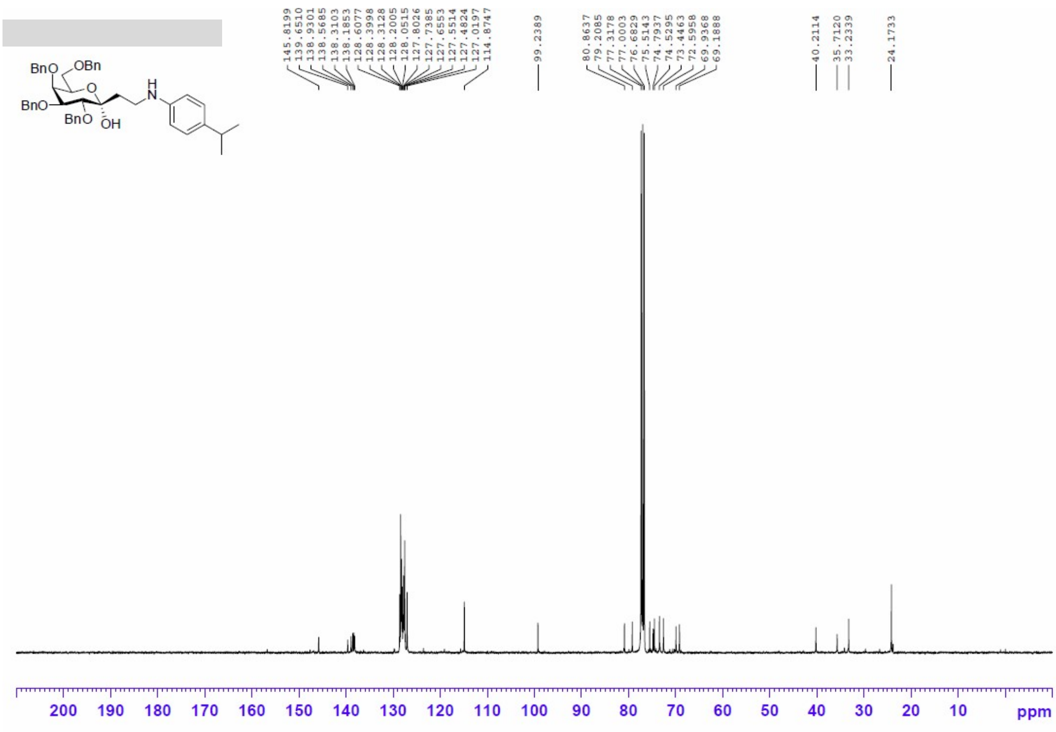
^{13}C NMR spectra of **3n**



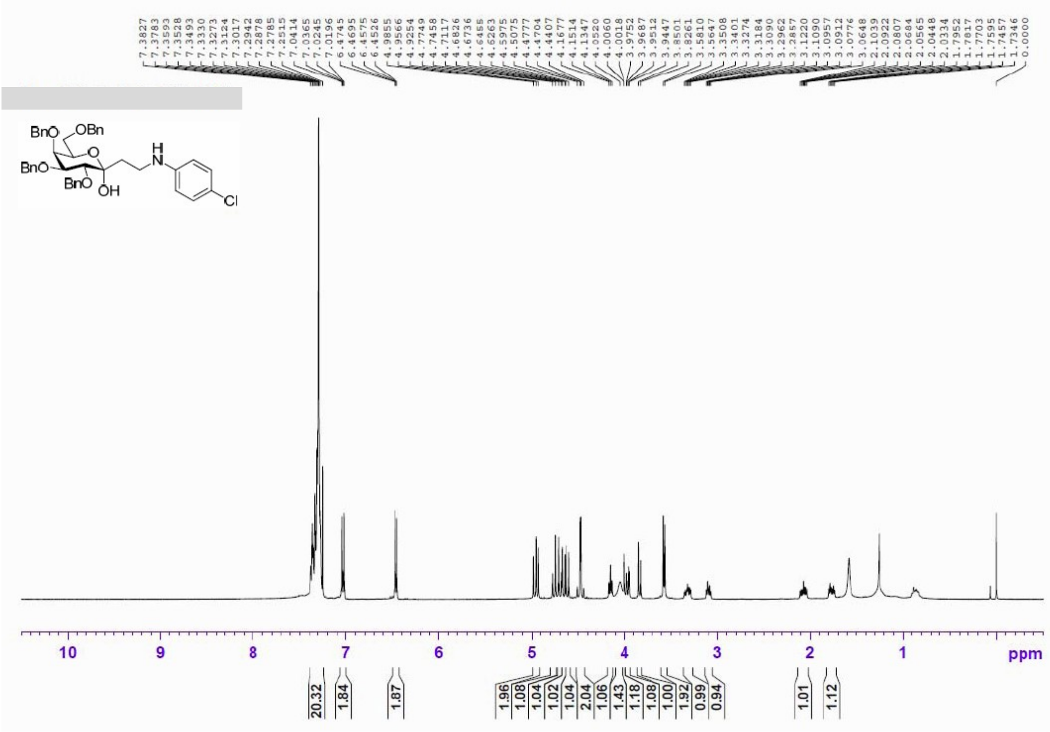
[1]H NMR spectrum of **3o**



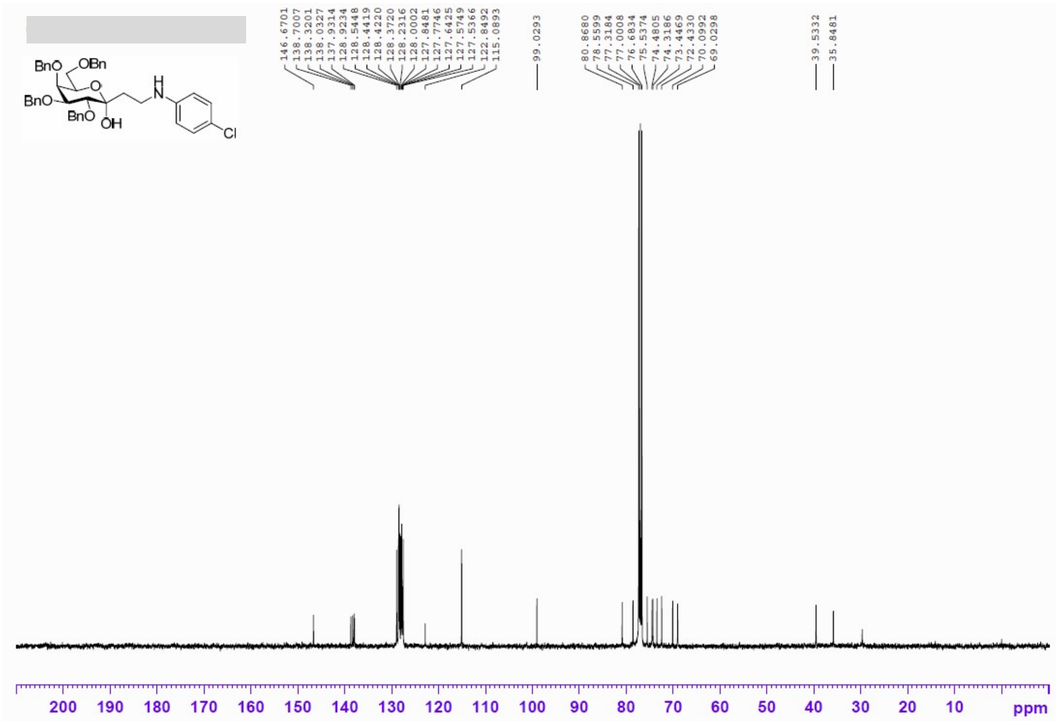
[13]C NMR spectra of **3o**



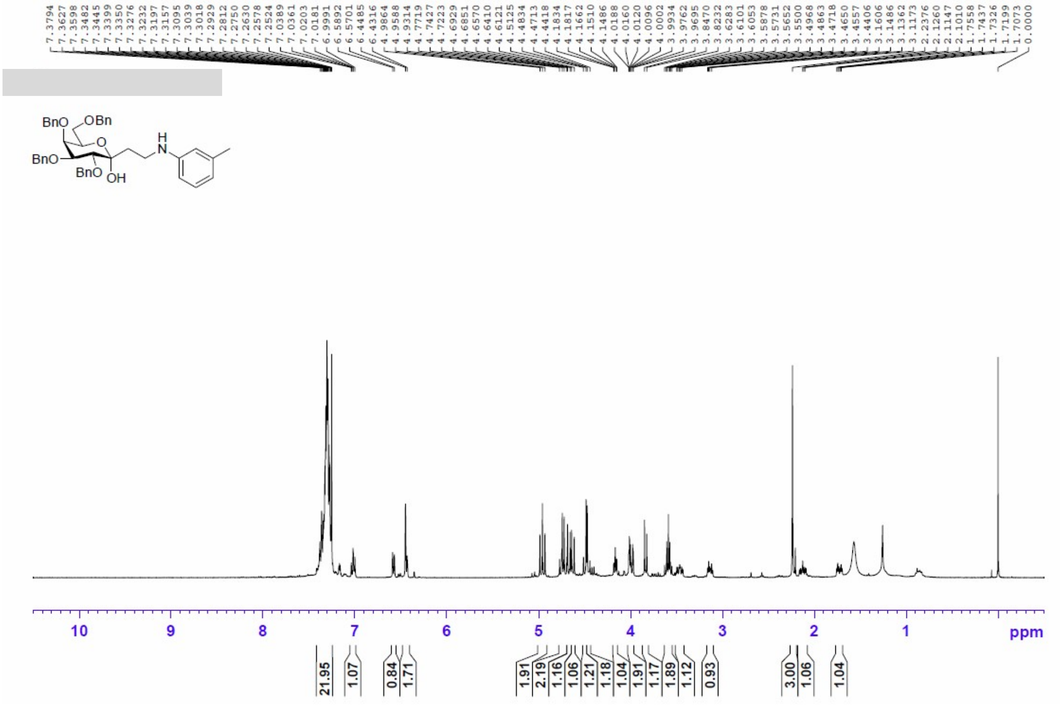
[1]H NMR spectrum of **3p**



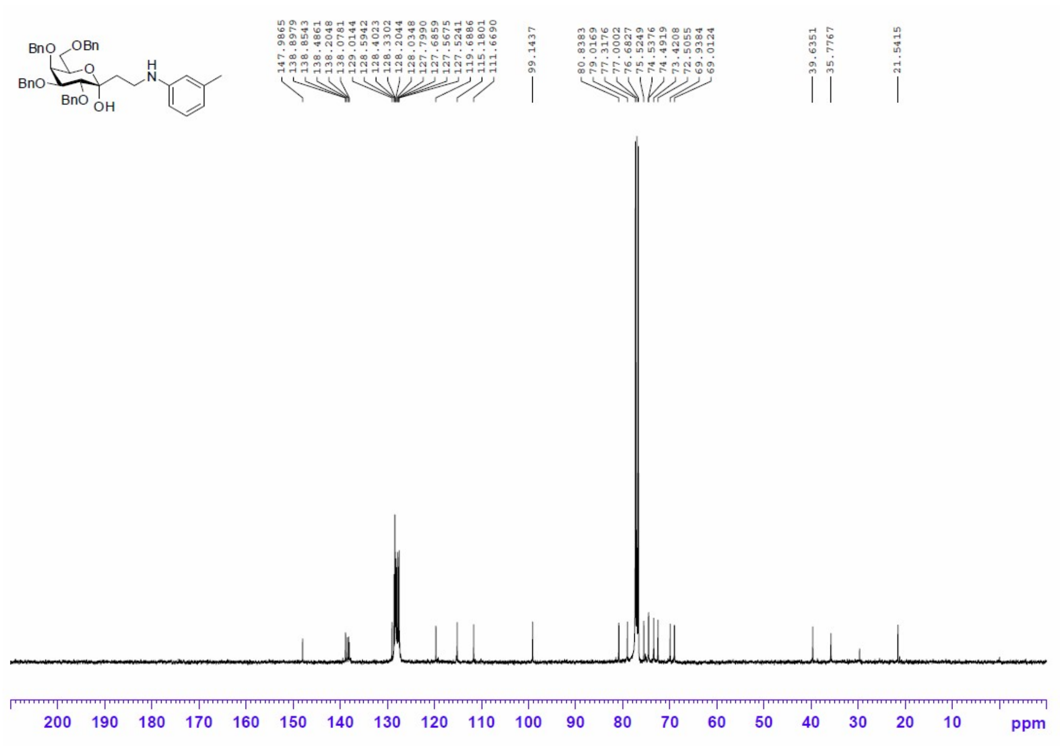
[13]C NMR spectra of **3p**



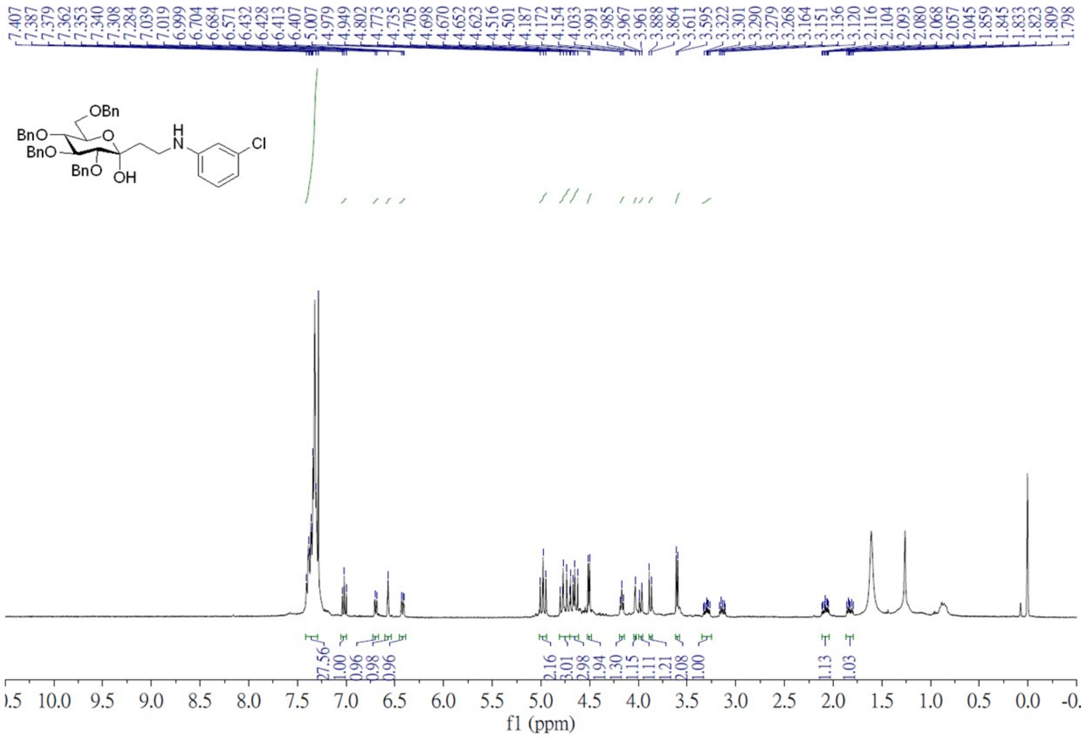
[1]H NMR spectrum of **3q**



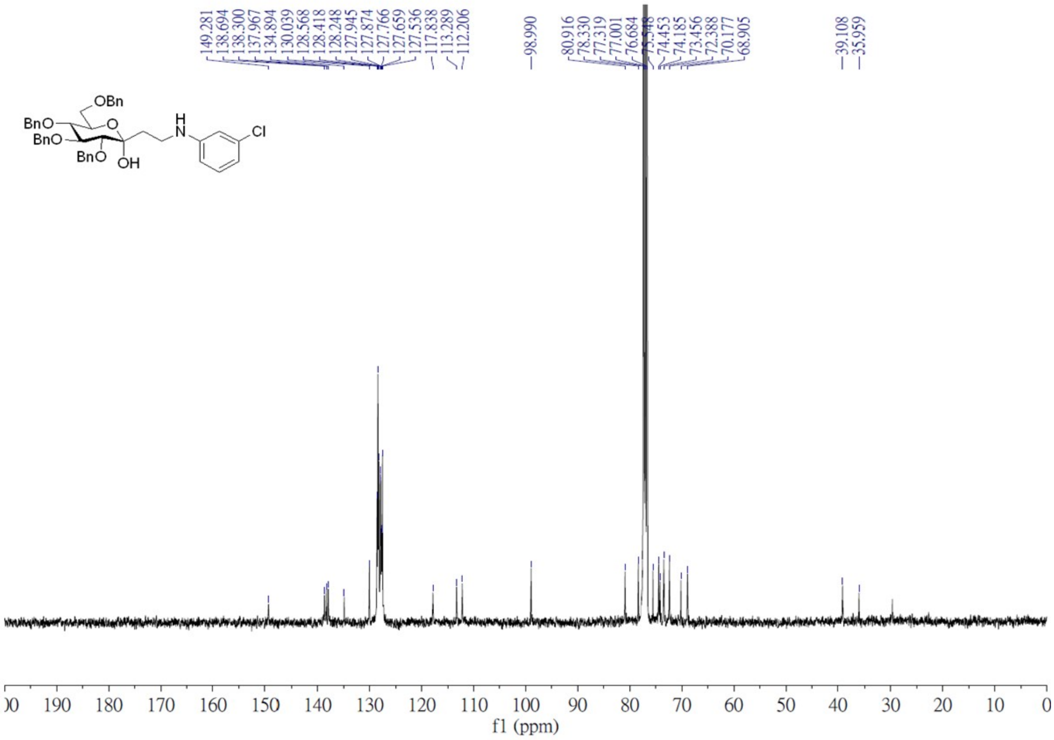
[13]C NMR spectra of **3q**



[1]H NMR spectrum of **3r**

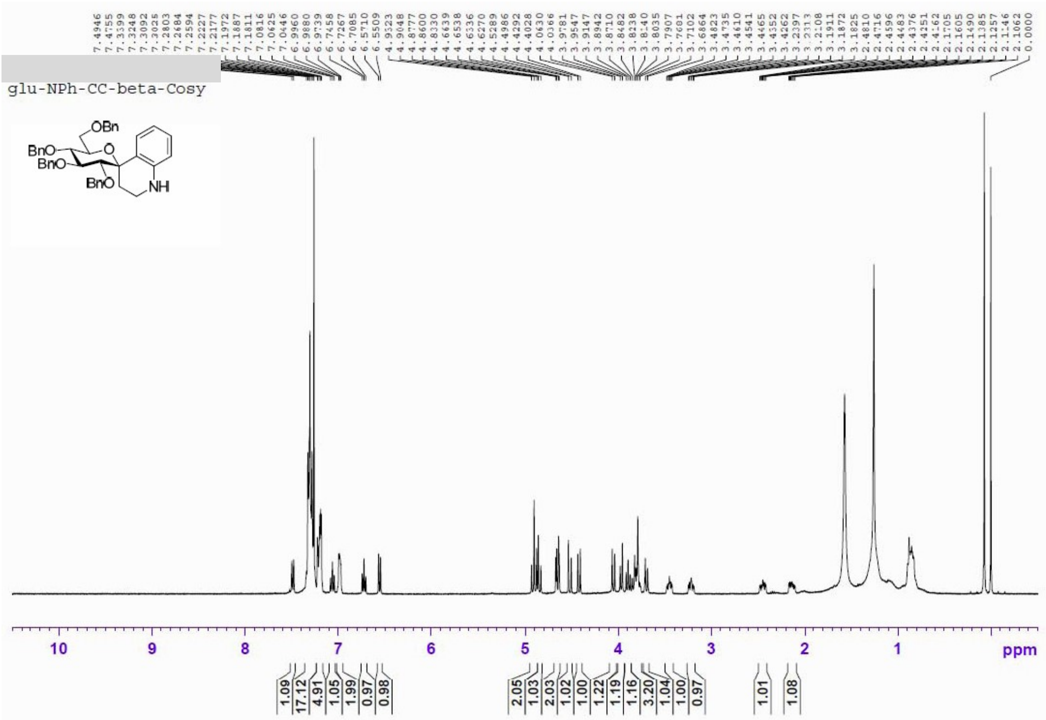


[13]C NMR spectra of **3r**

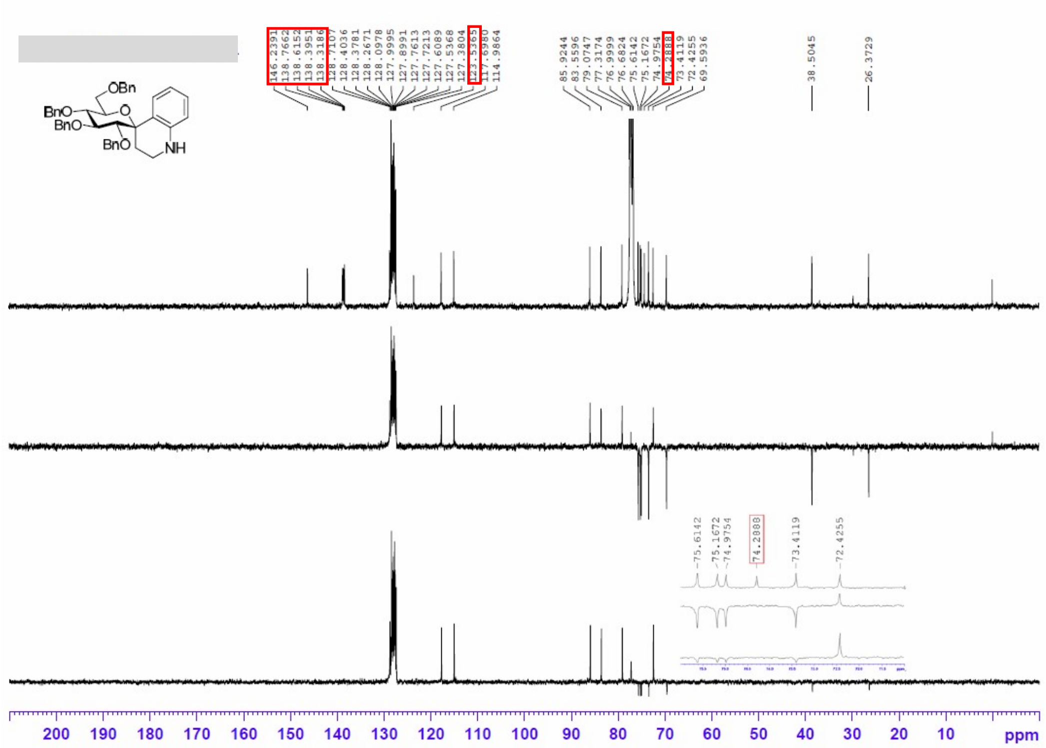


^{1}H and ^{13}C NMR spectra of 4a-4y

^{1}H NMR spectrum of **4a**

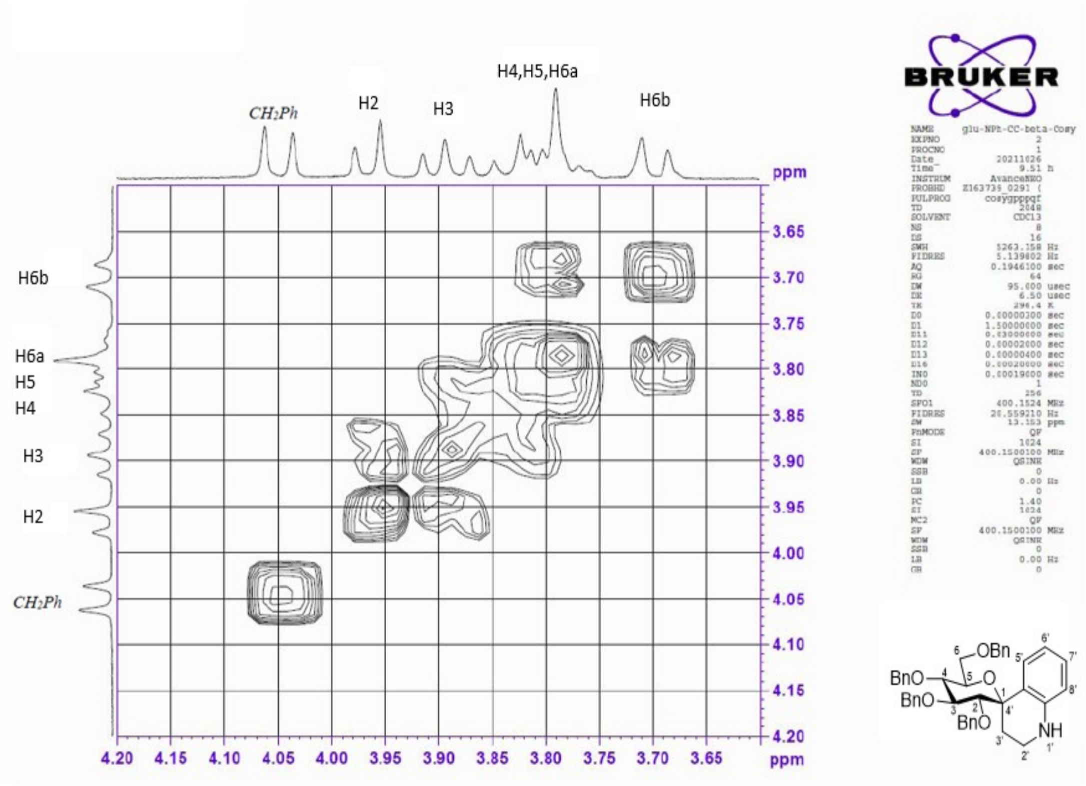


^{13}C NMR spectra of **4a**

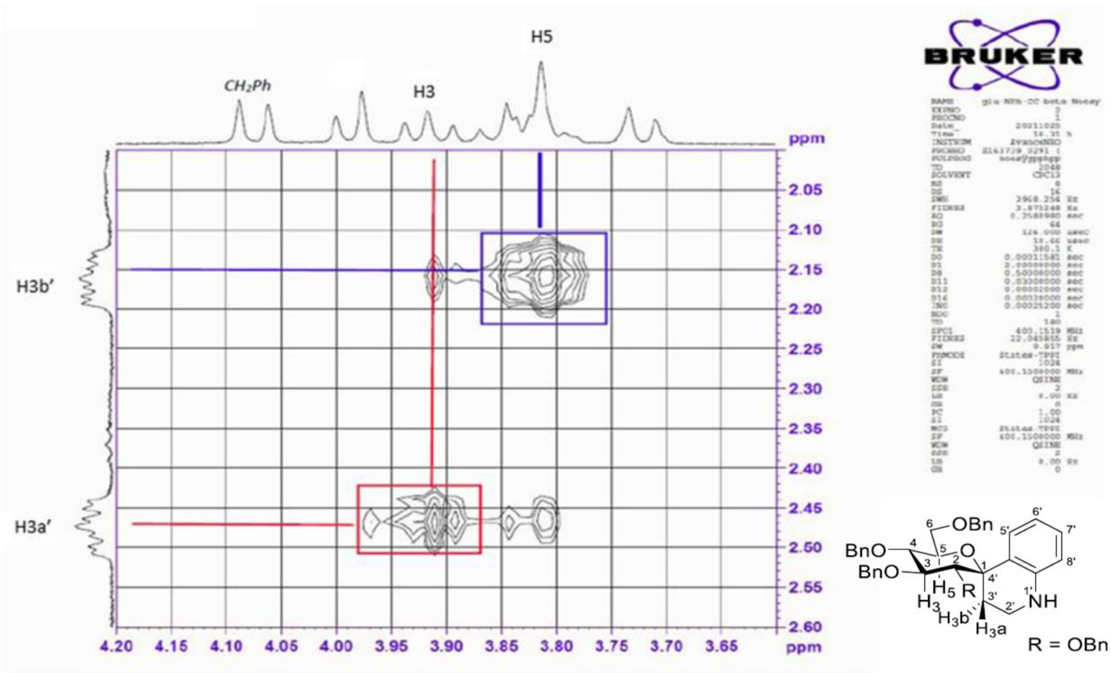


2D NMR spectra of 4a

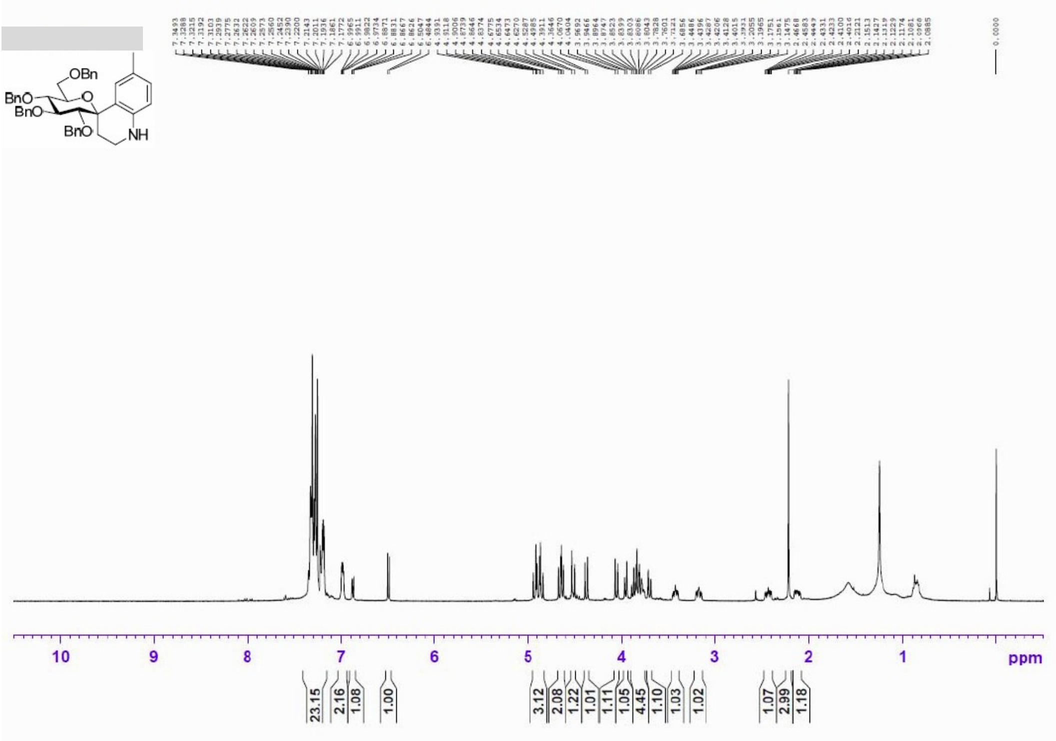
H-H COSY NMR spectrum of **4a**



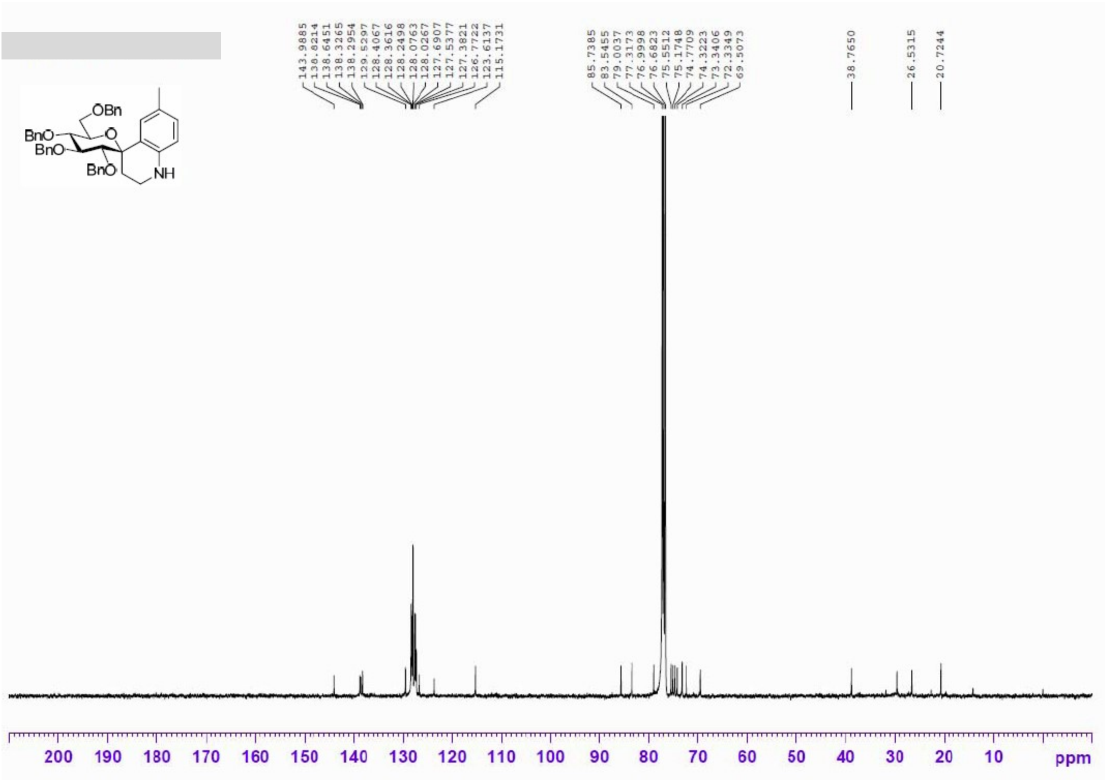
NOESY NMR spectrum of **4a**



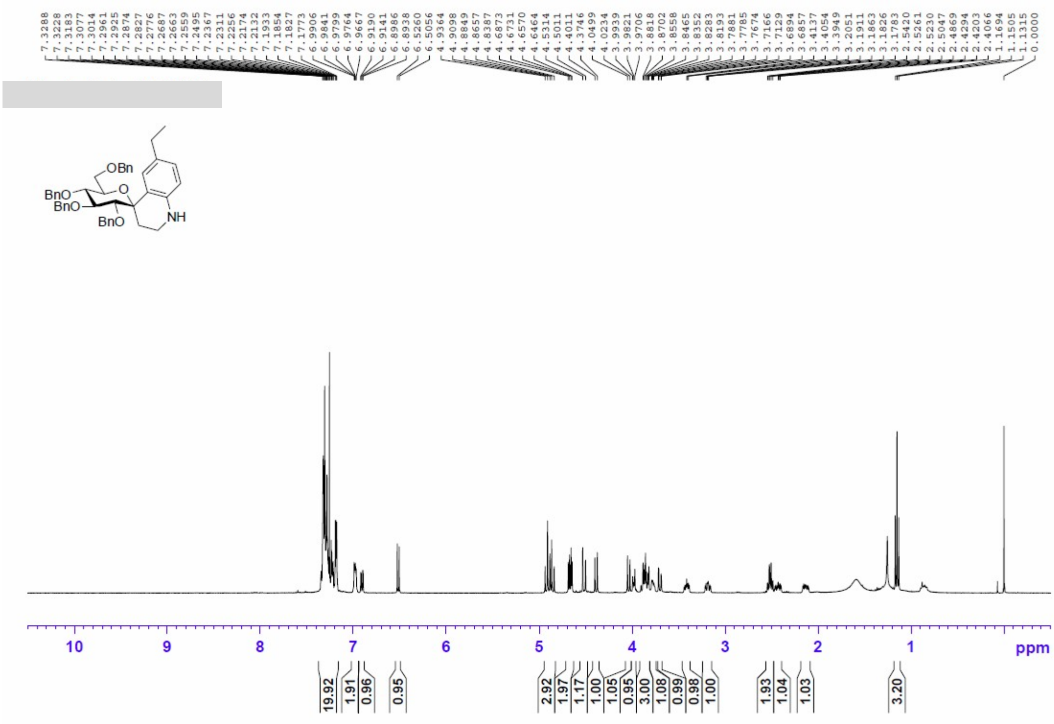
[1]H NMR spectrum of **4b**



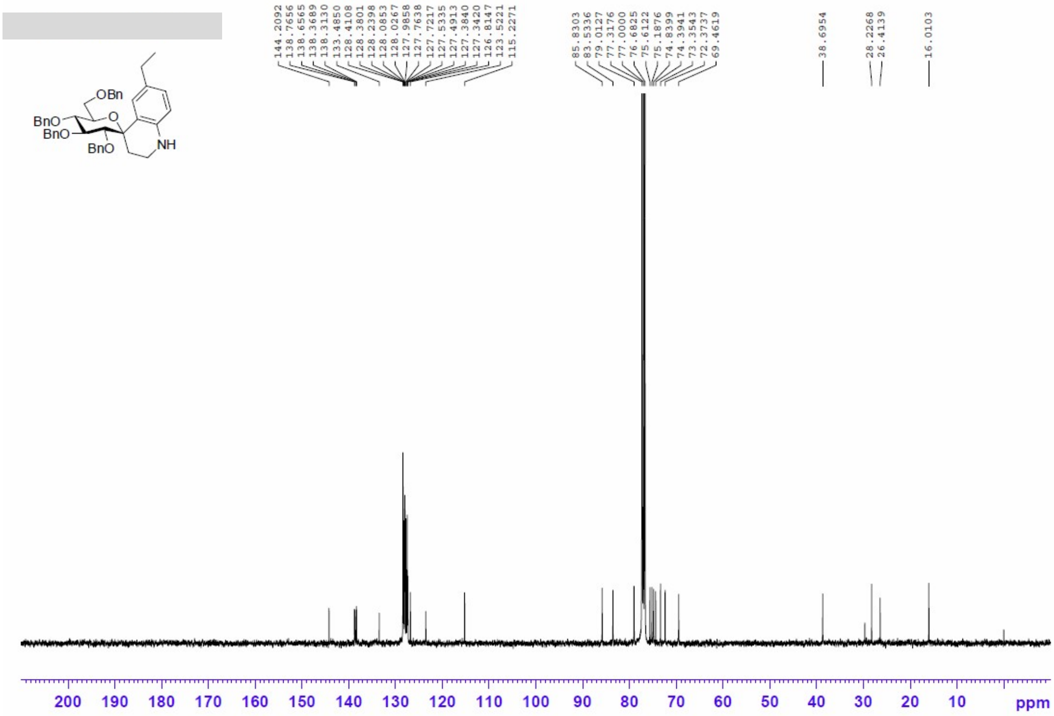
[13]C NMR spectra of **4b**



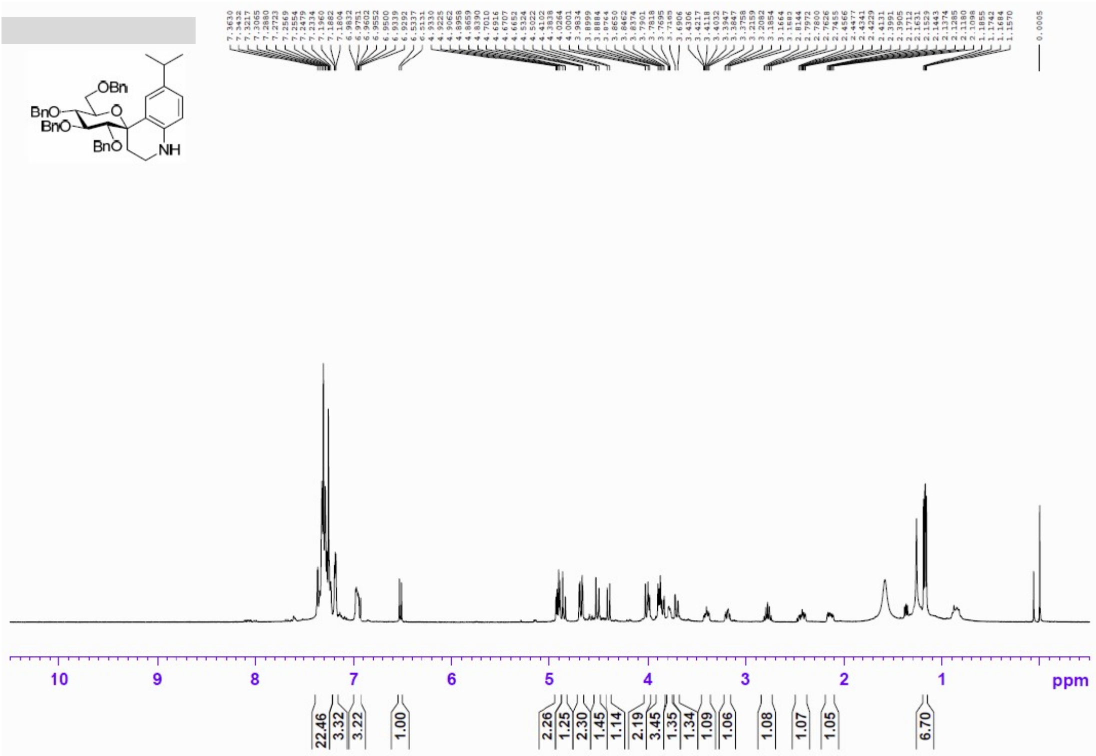
^{1}H NMR spectrum of **4c**



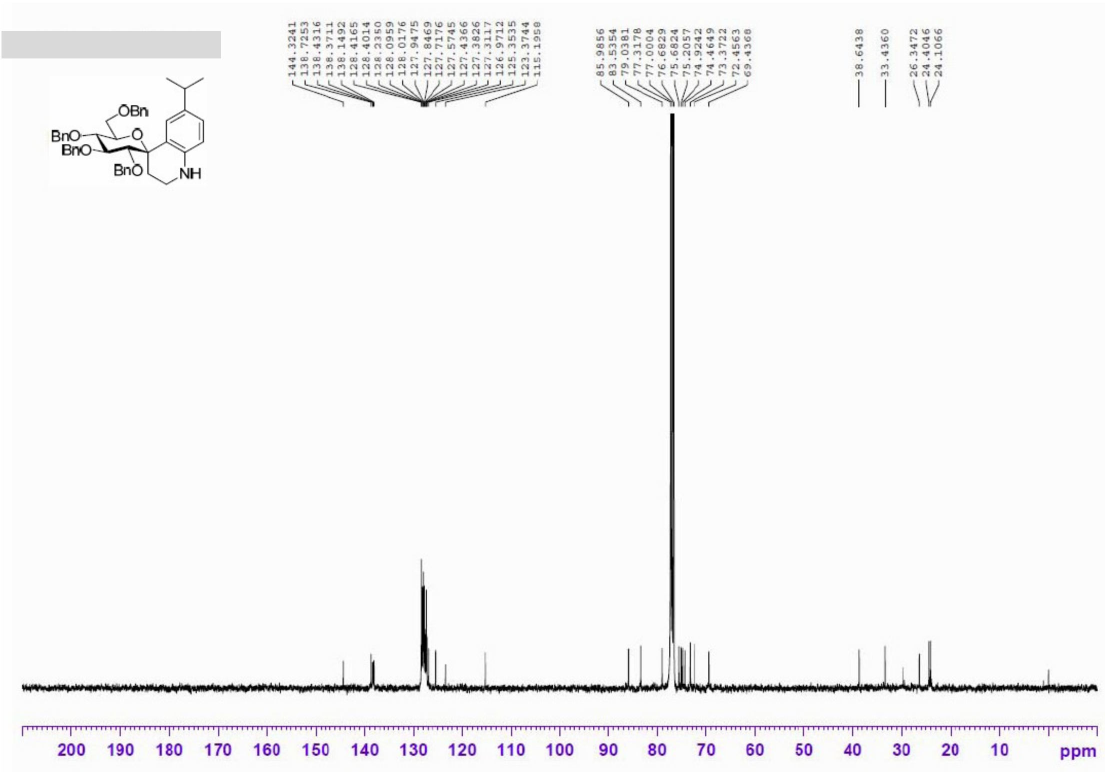
^{13}C NMR spectra of **4c**



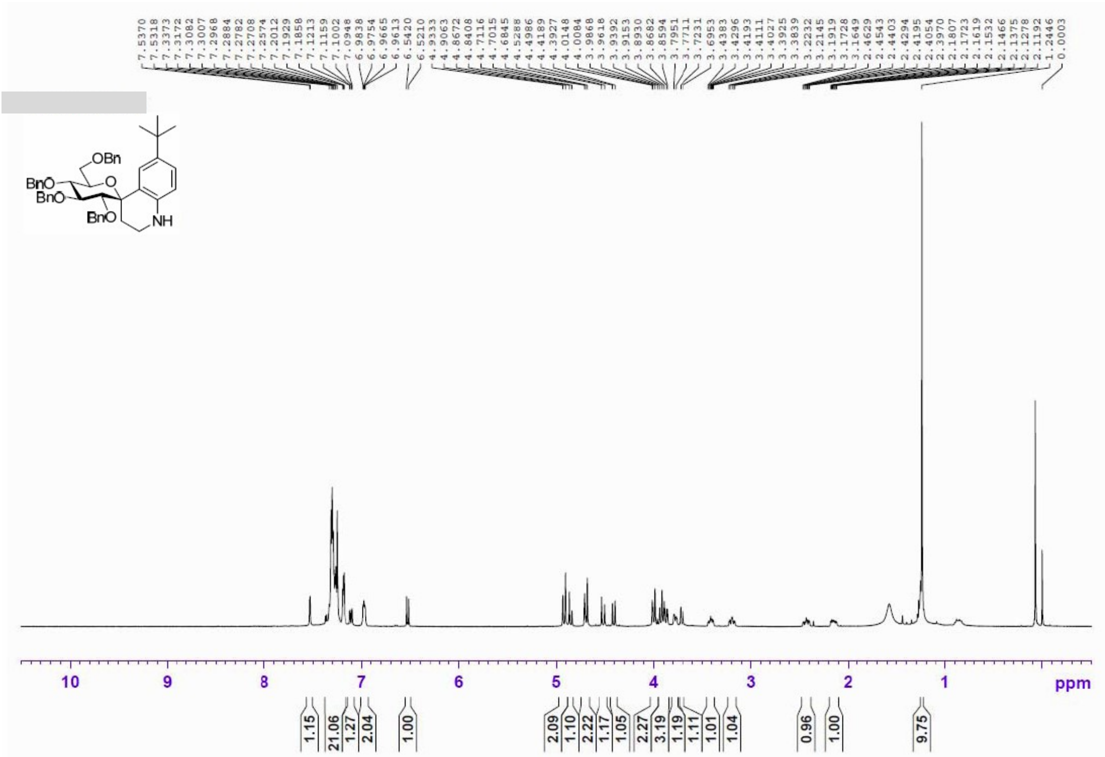
[1]H NMR spectrum of **4d**



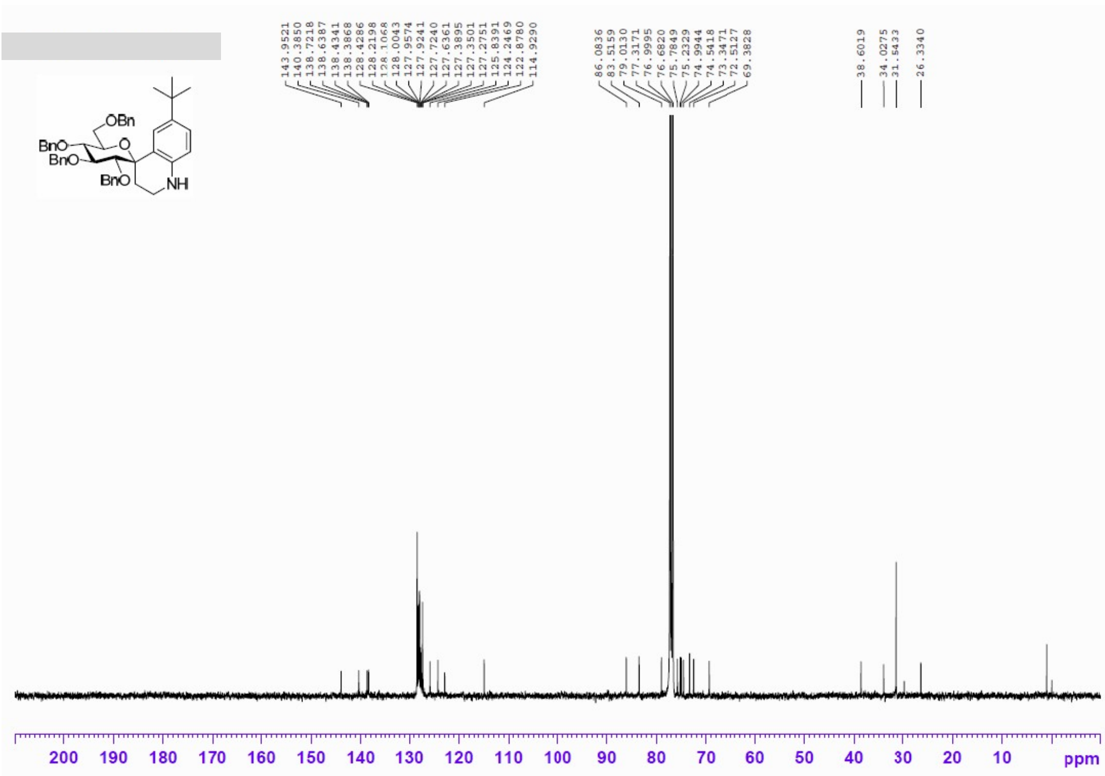
[13]C NMR spectra of **4d**



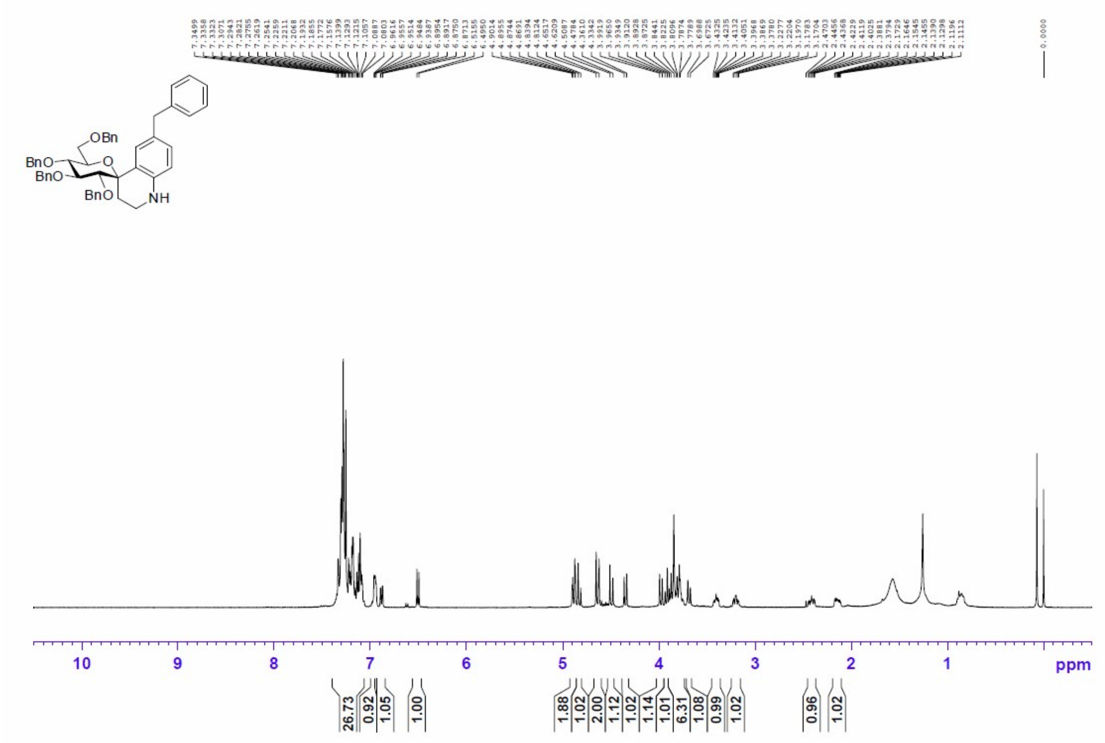
^{1}H NMR spectrum of **4e**



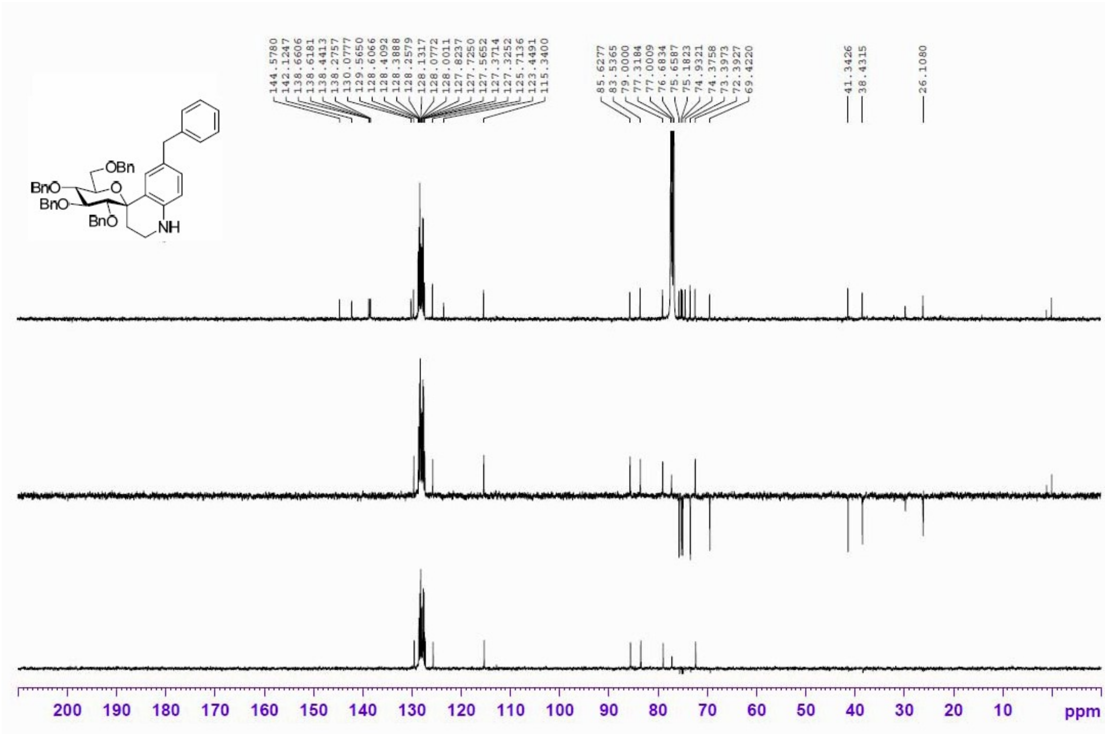
^{13}C NMR spectra of **4e**



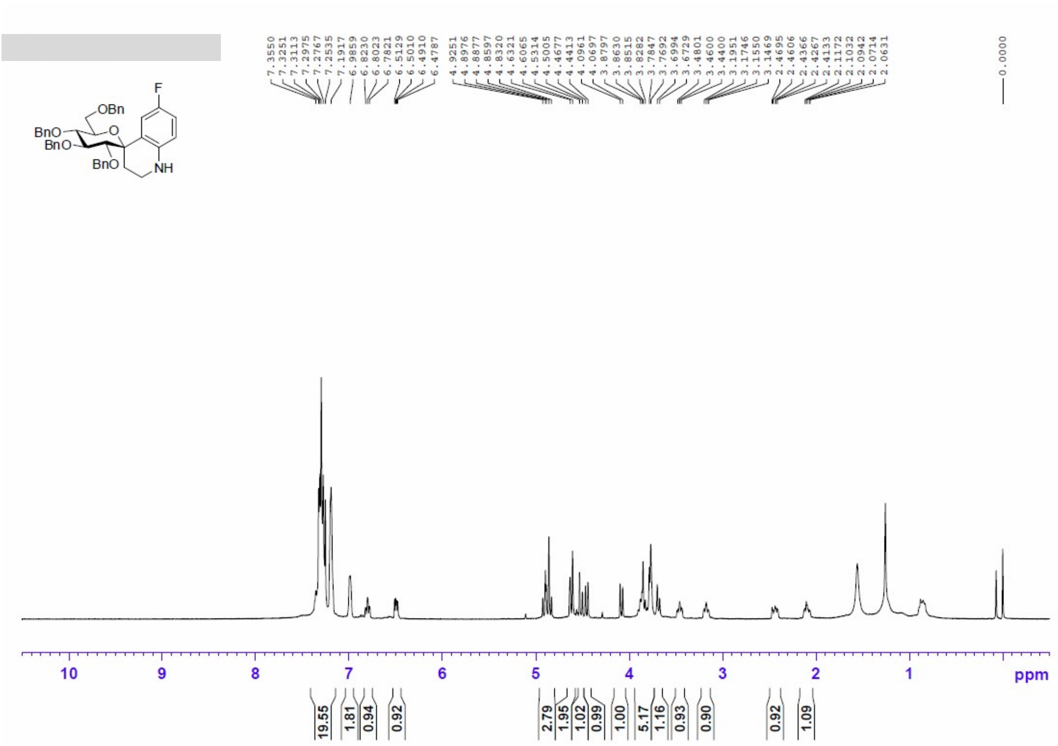
[1]H NMR spectrum of **4f**



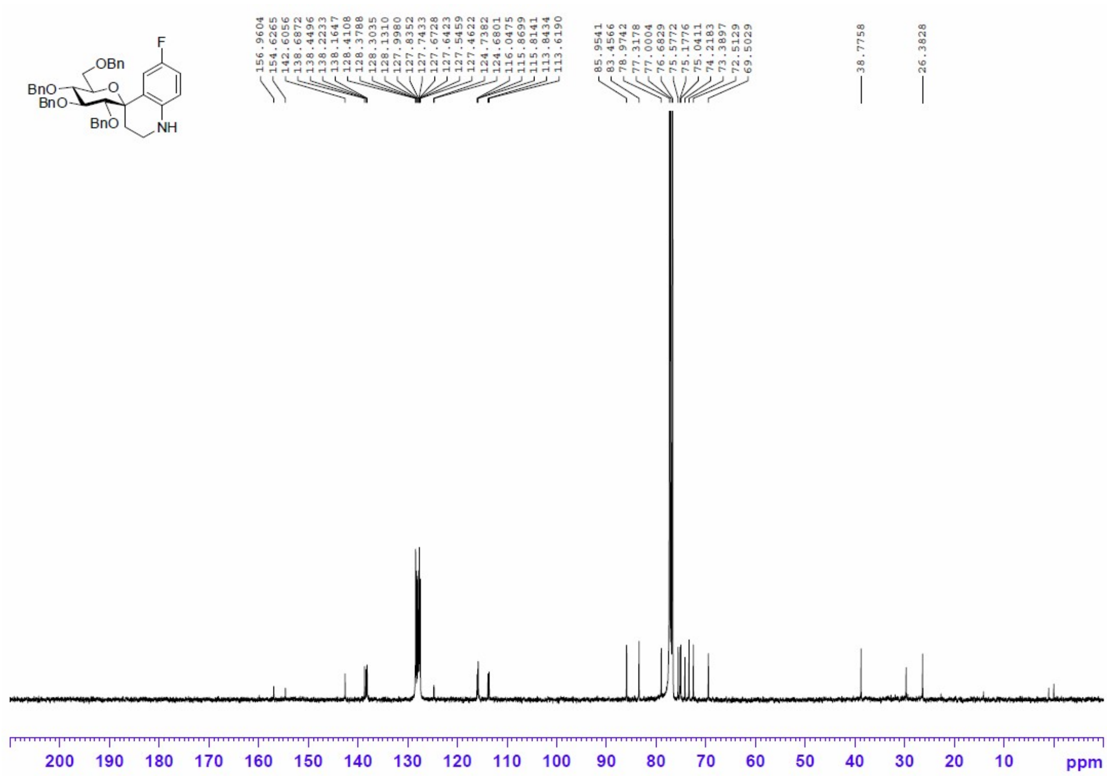
[13]C NMR spectra of **4f**



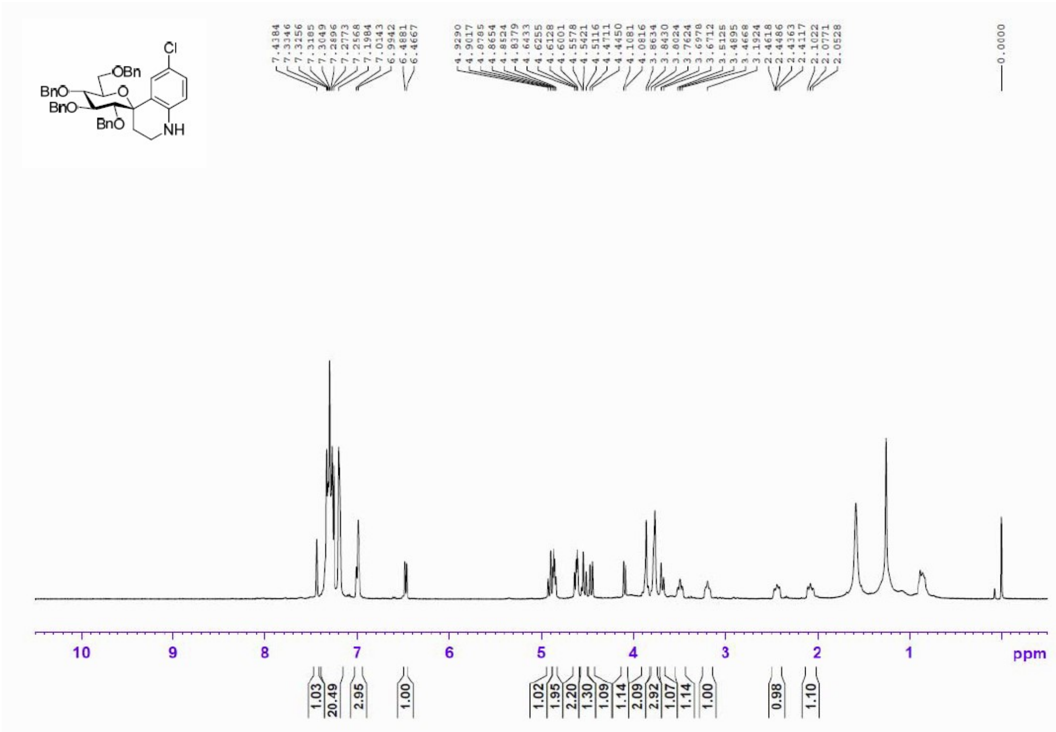
^{1}H NMR spectrum of **4g**



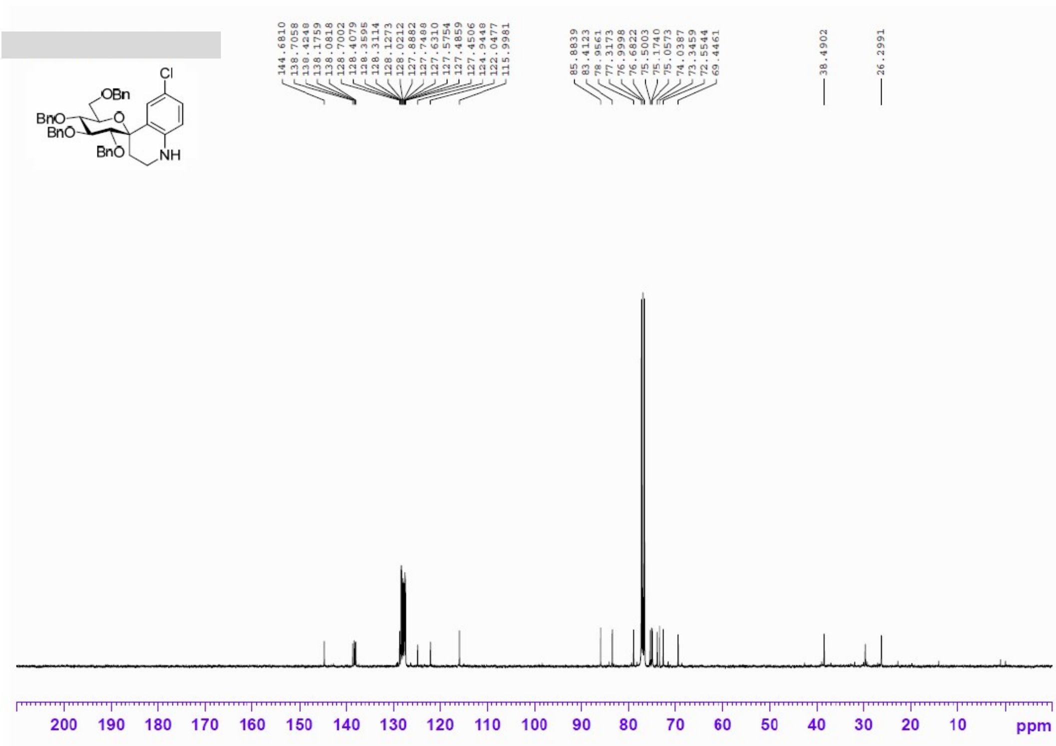
^{13}C NMR spectra of **4g**



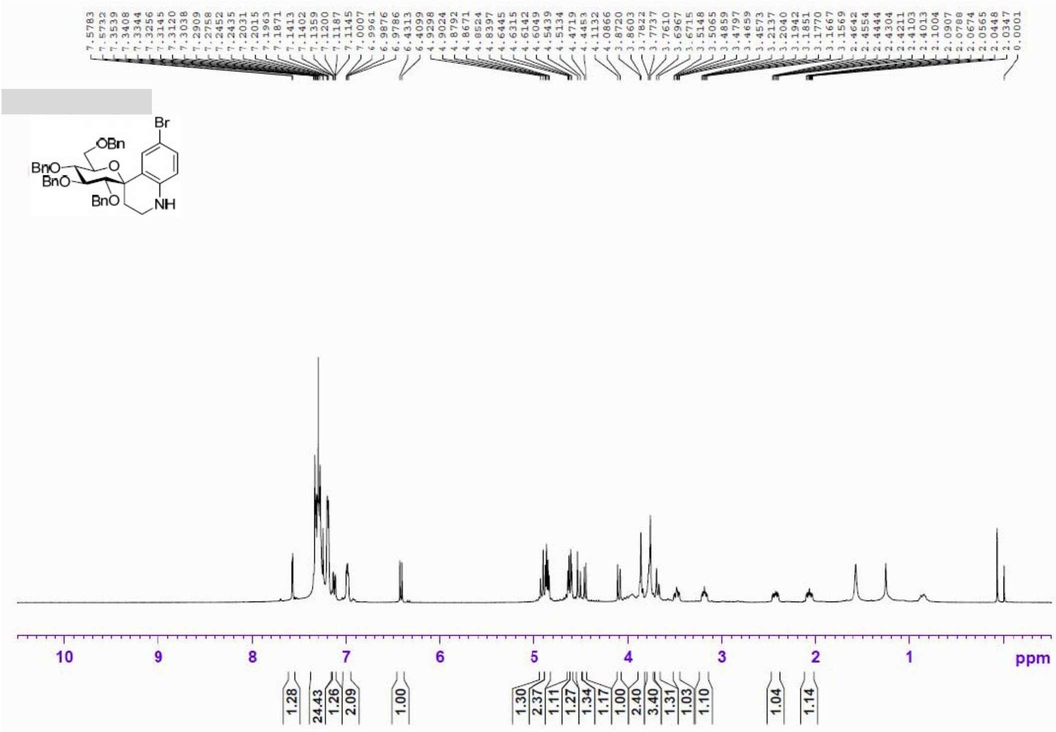
[1]H NMR spectrum of **4h**



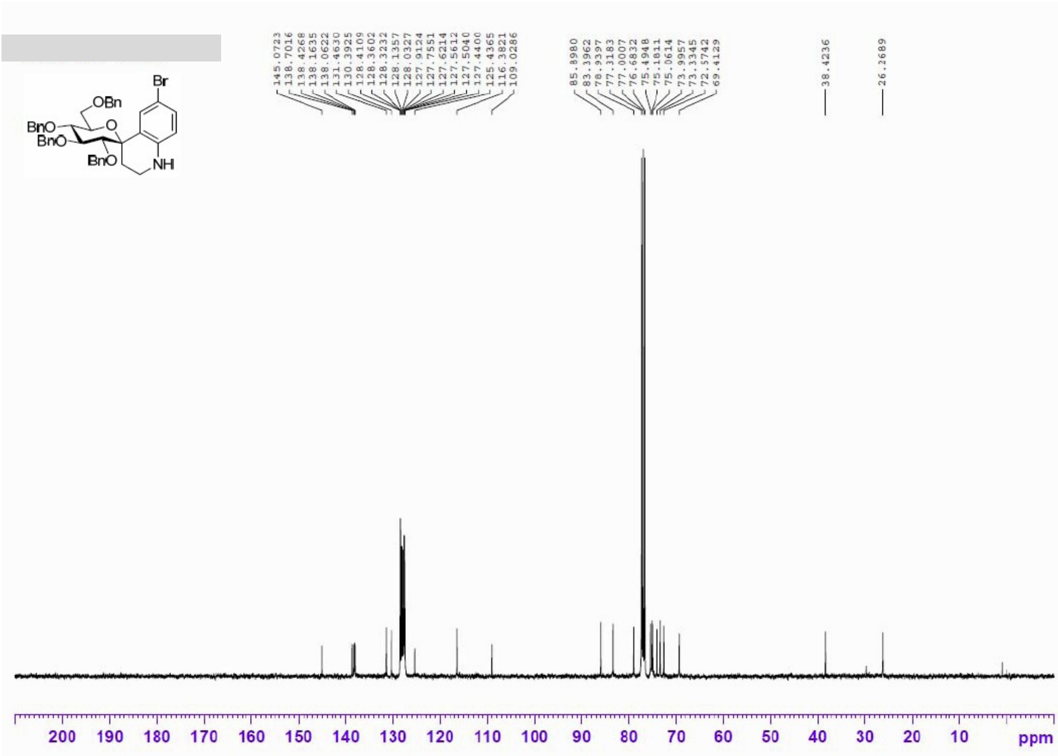
[13]C NMR spectra of **4h**



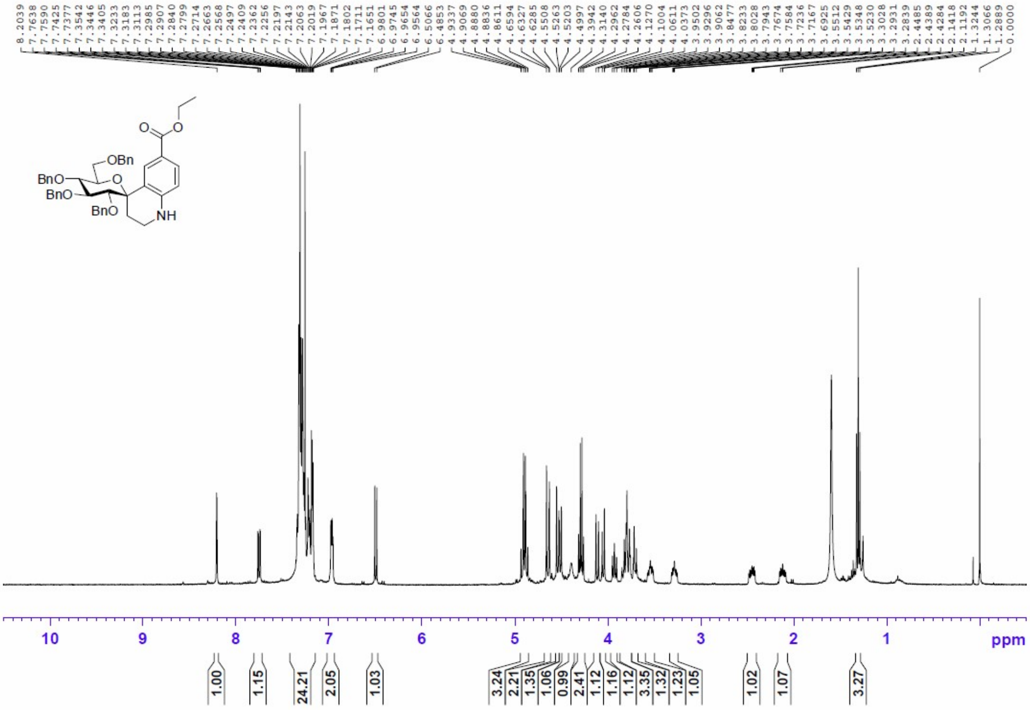
[1]H NMR spectrum of **4i**



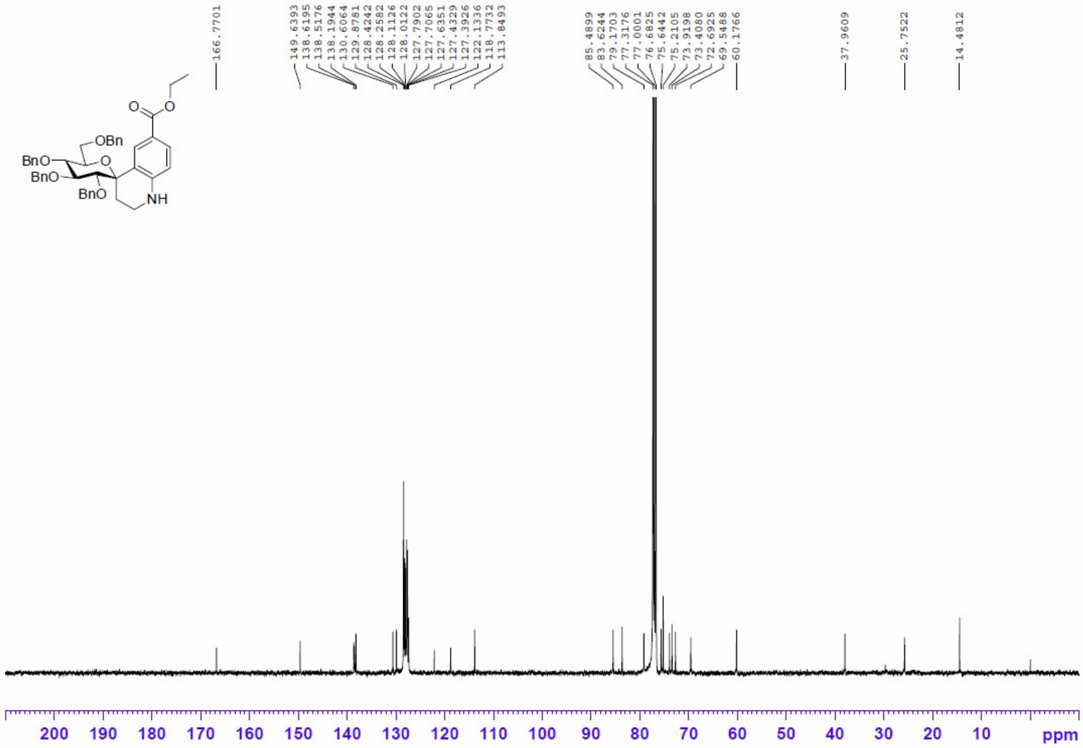
[13]C NMR spectra of **4i**



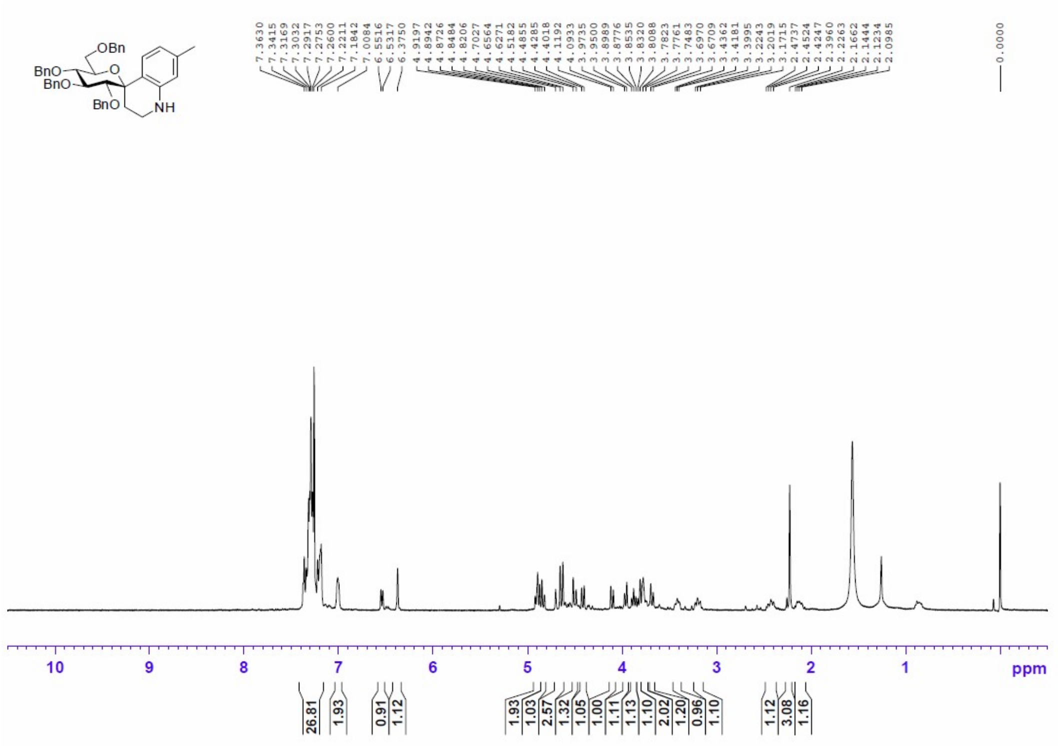
[1]H NMR spectrum of **4j**



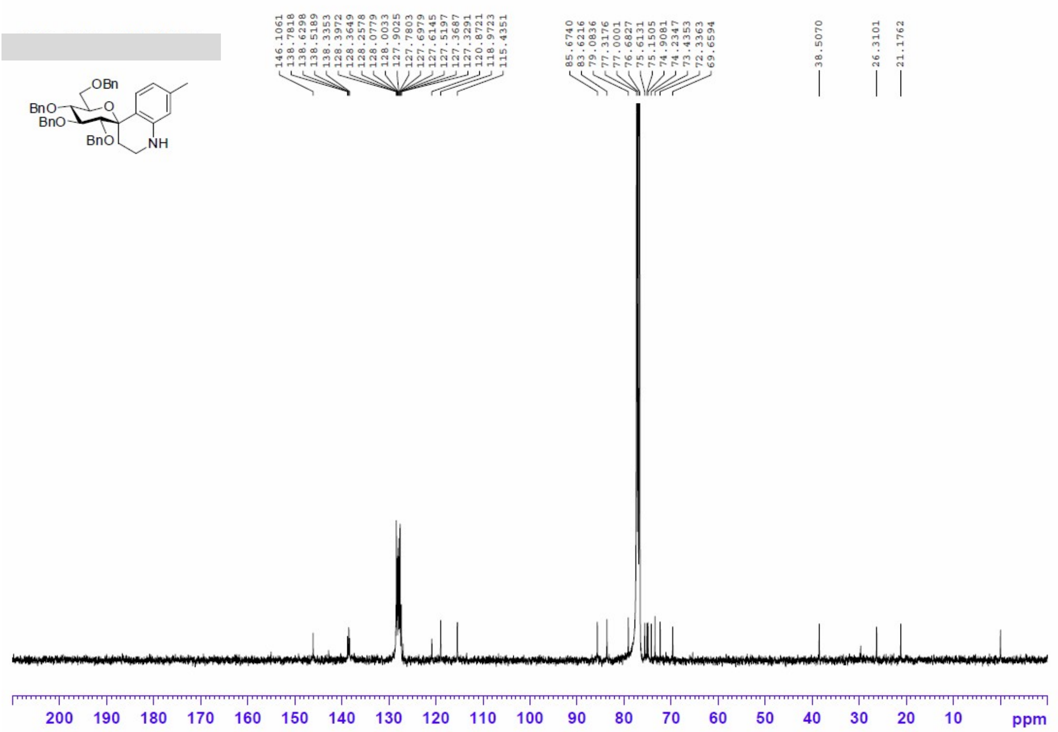
[13]C NMR spectra of **4j**



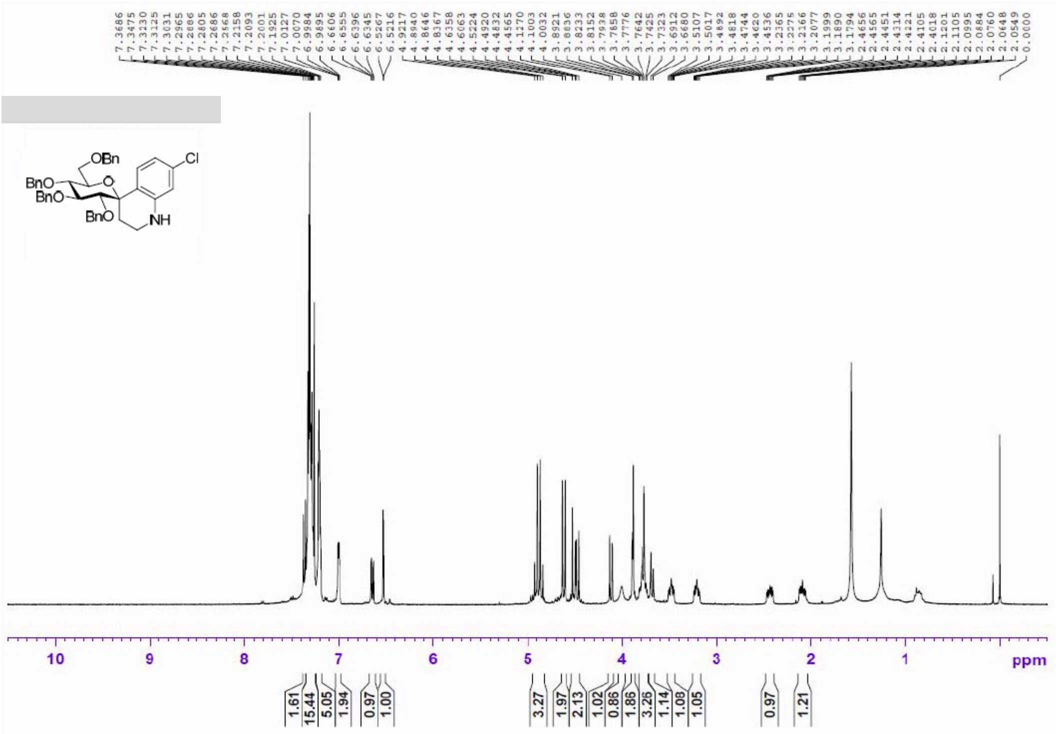
[1]H NMR spectrum of **4k**



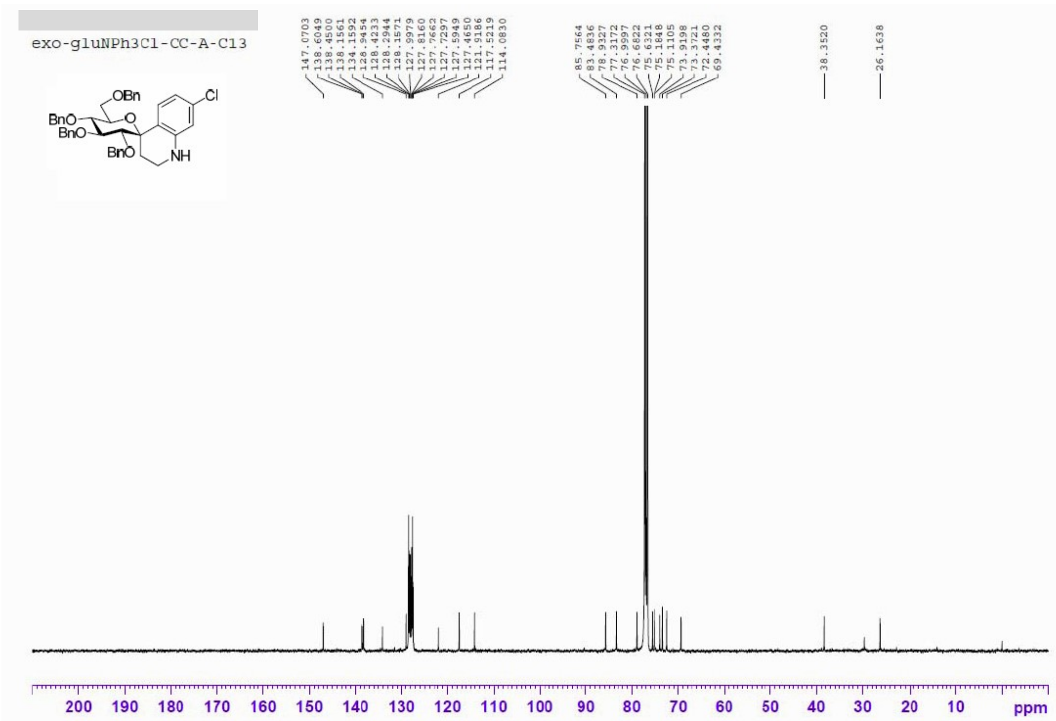
[13]C NMR spectra of **4k**



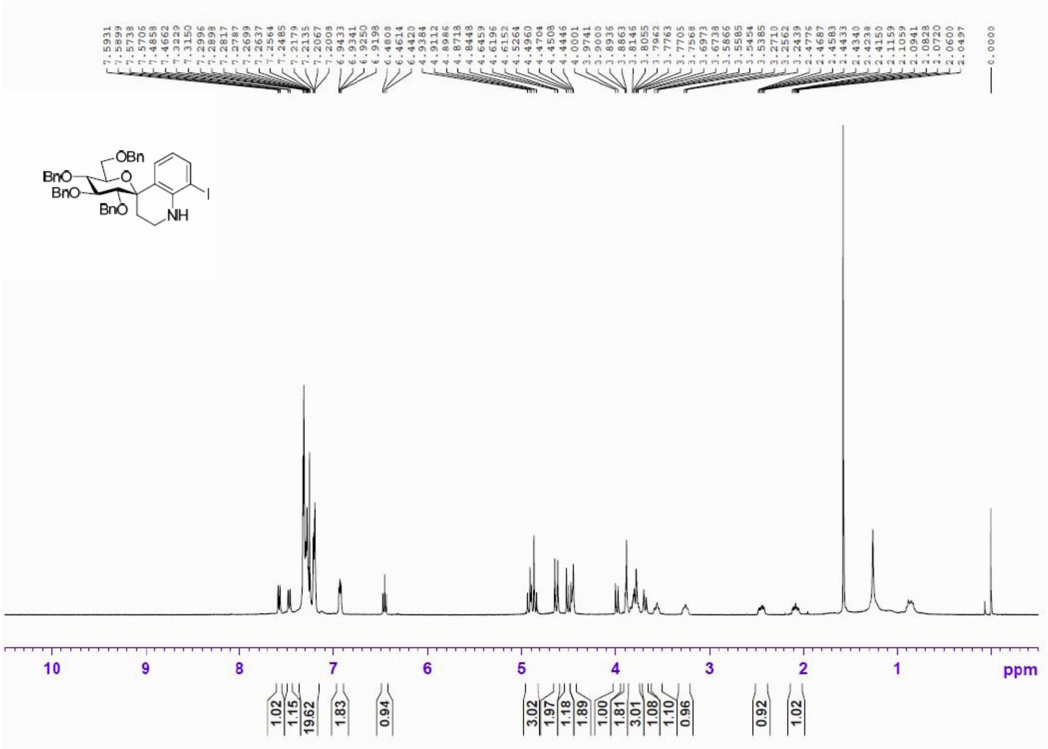
^{1}H NMR spectrum of **4l**



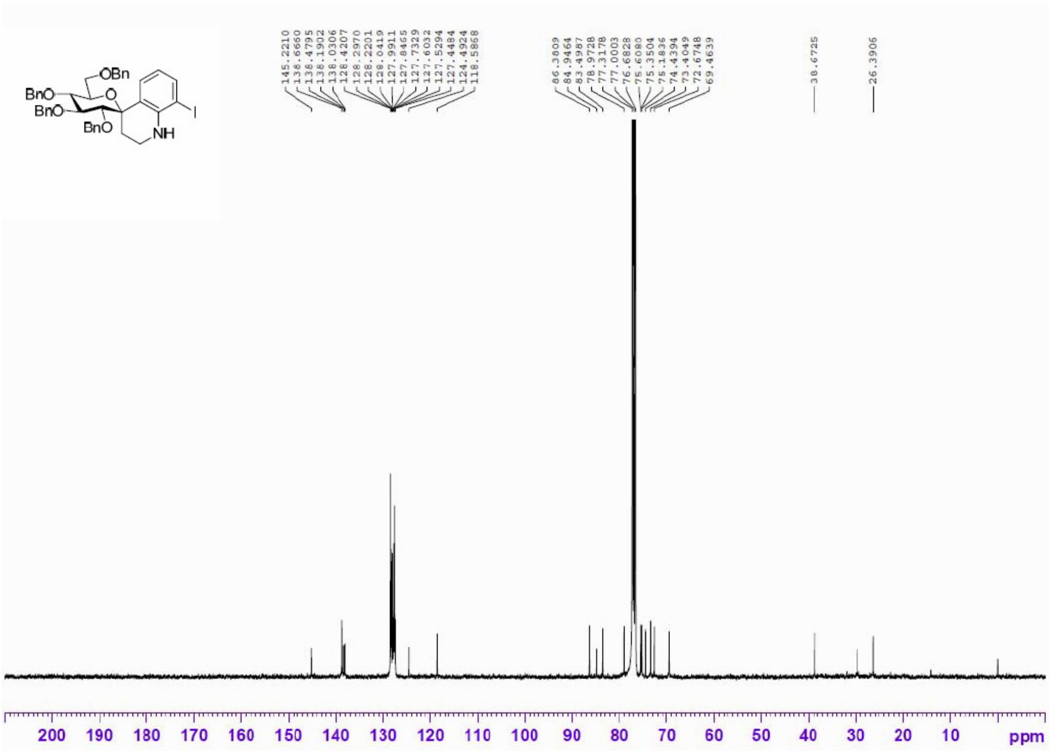
^{13}C NMR spectra of **4l**



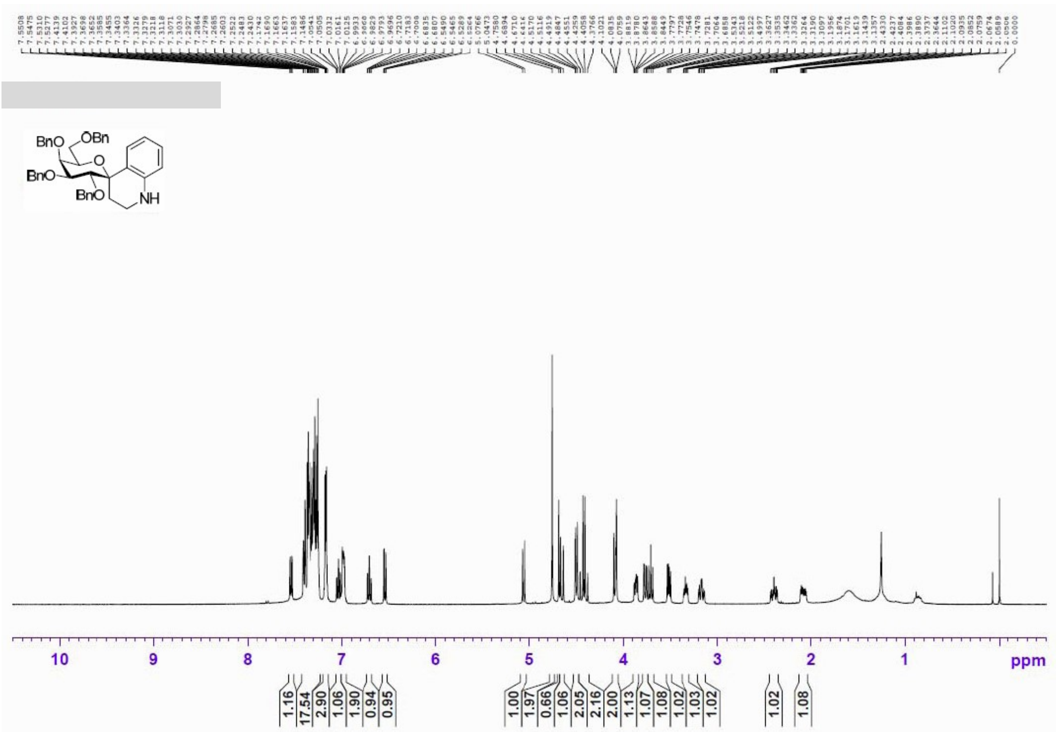
^{1}H NMR spectrum of **4m**



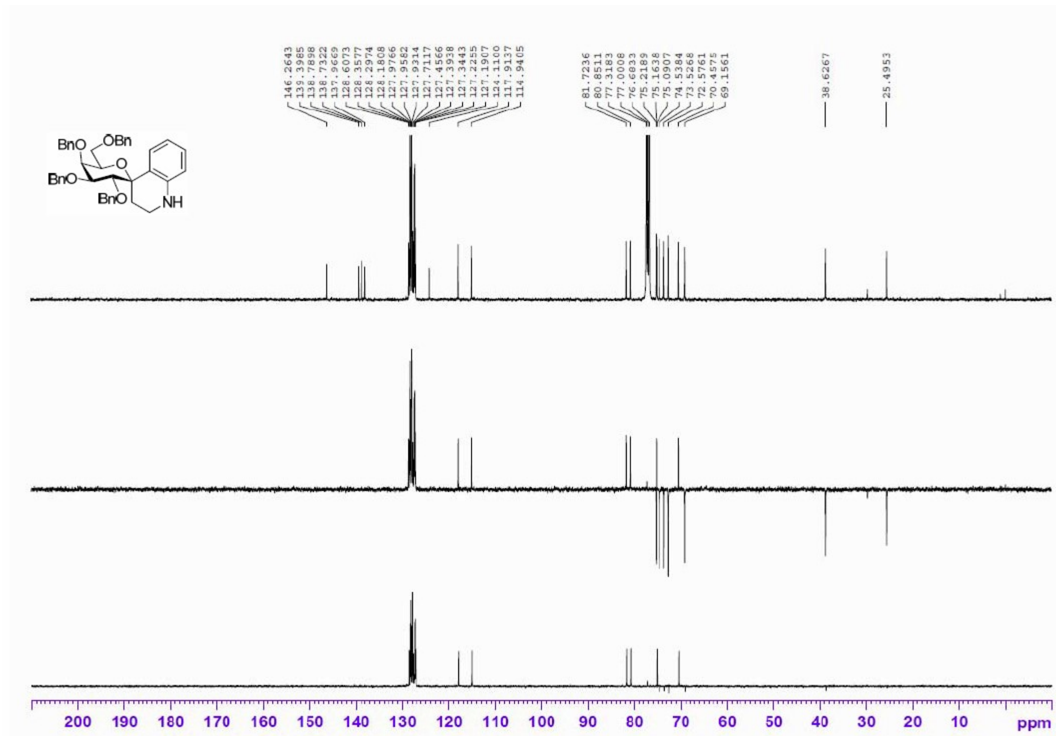
^{13}C NMR spectra of **4m**



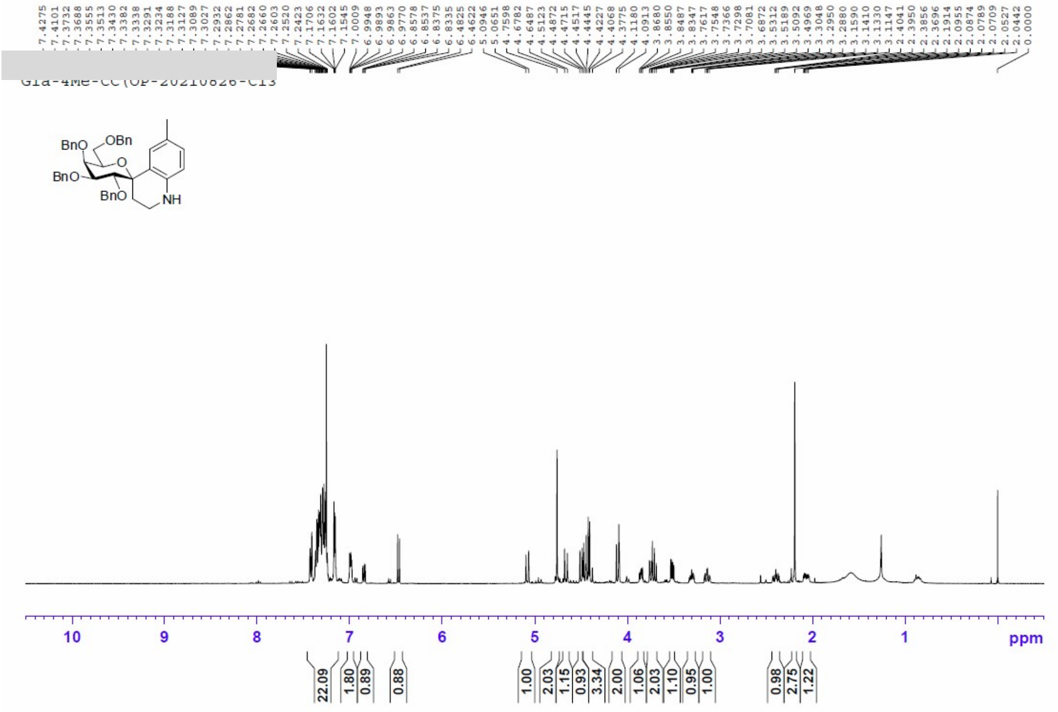
^{1}H NMR spectrum of **4n**



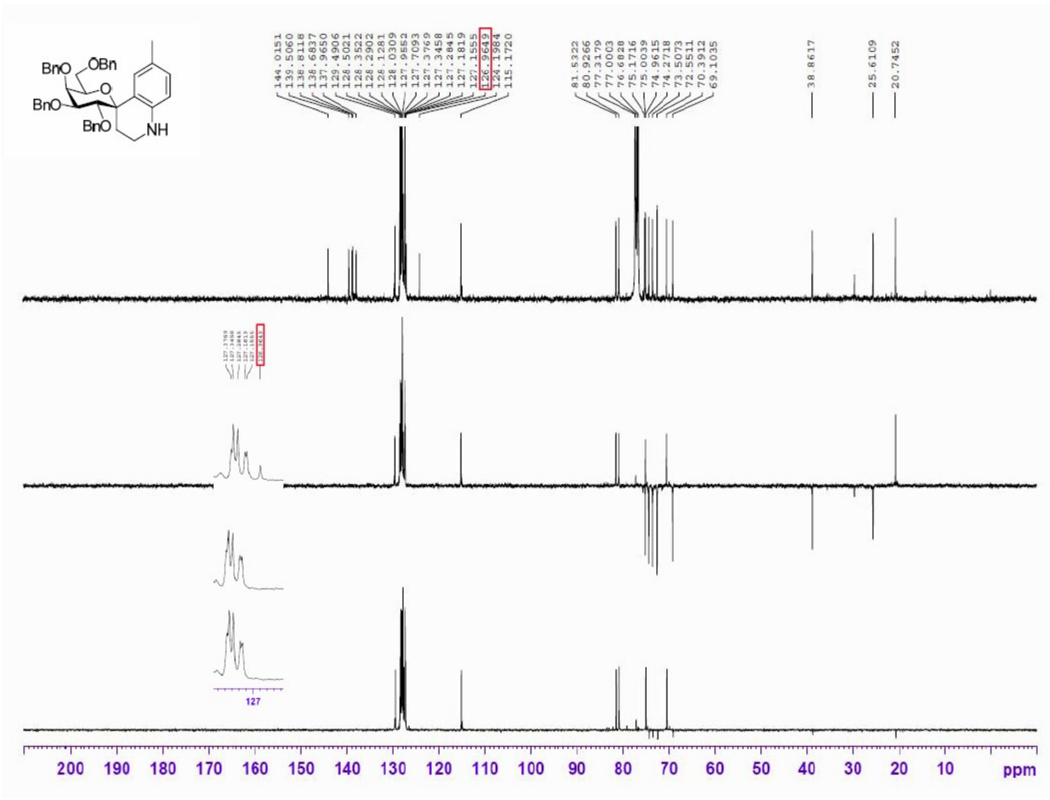
^{13}C NMR spectra of **4n**



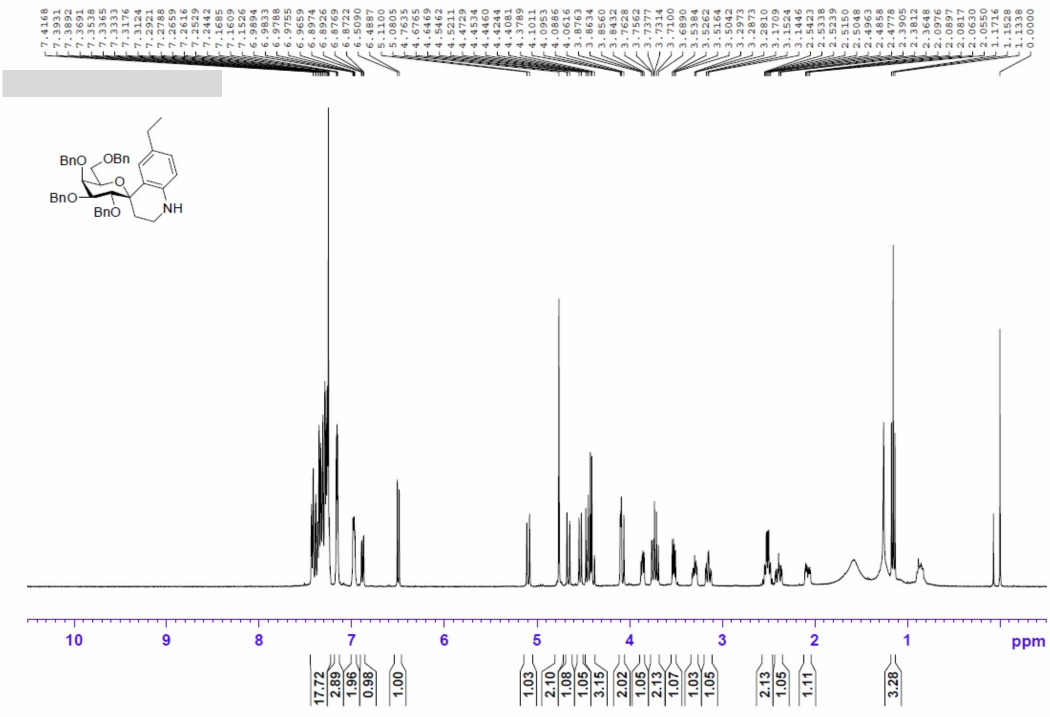
[1]H NMR spectrum of **4o**



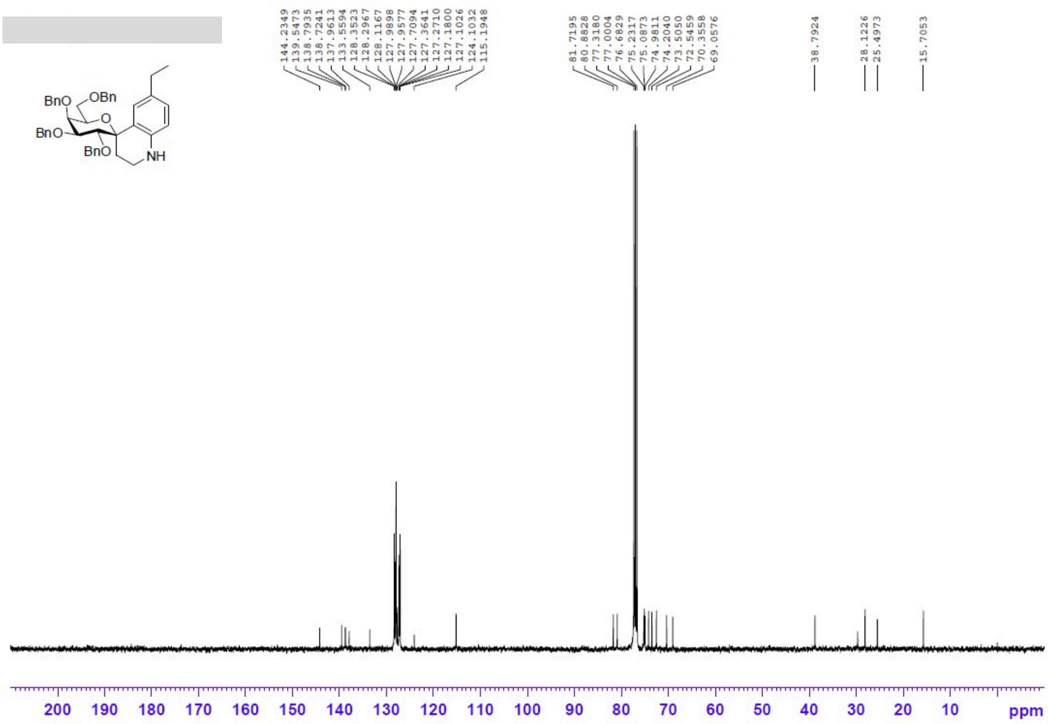
[13]C NMR spectra of **4o**



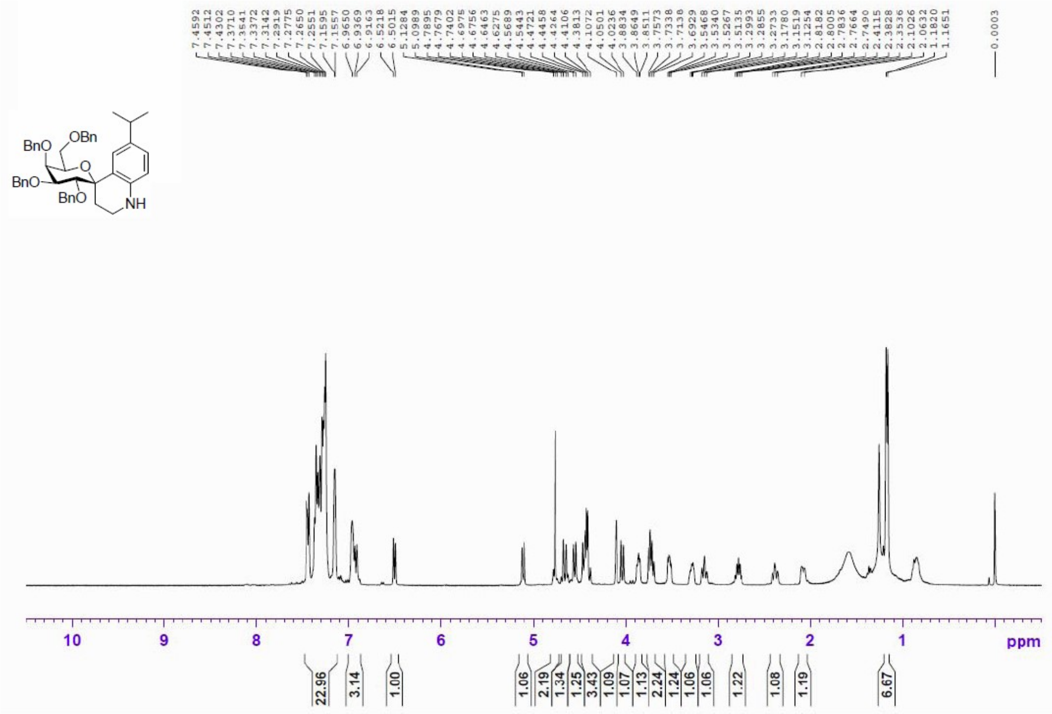
^{1}H NMR spectrum of **4p**



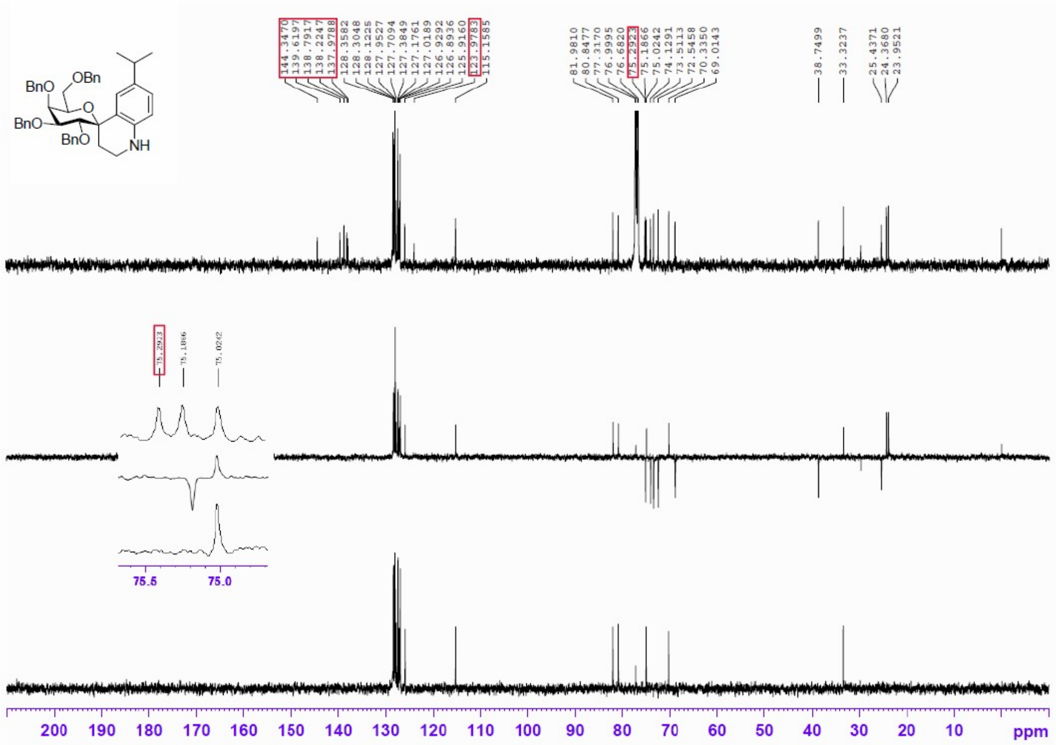
^{13}C NMR spectra of **4p**



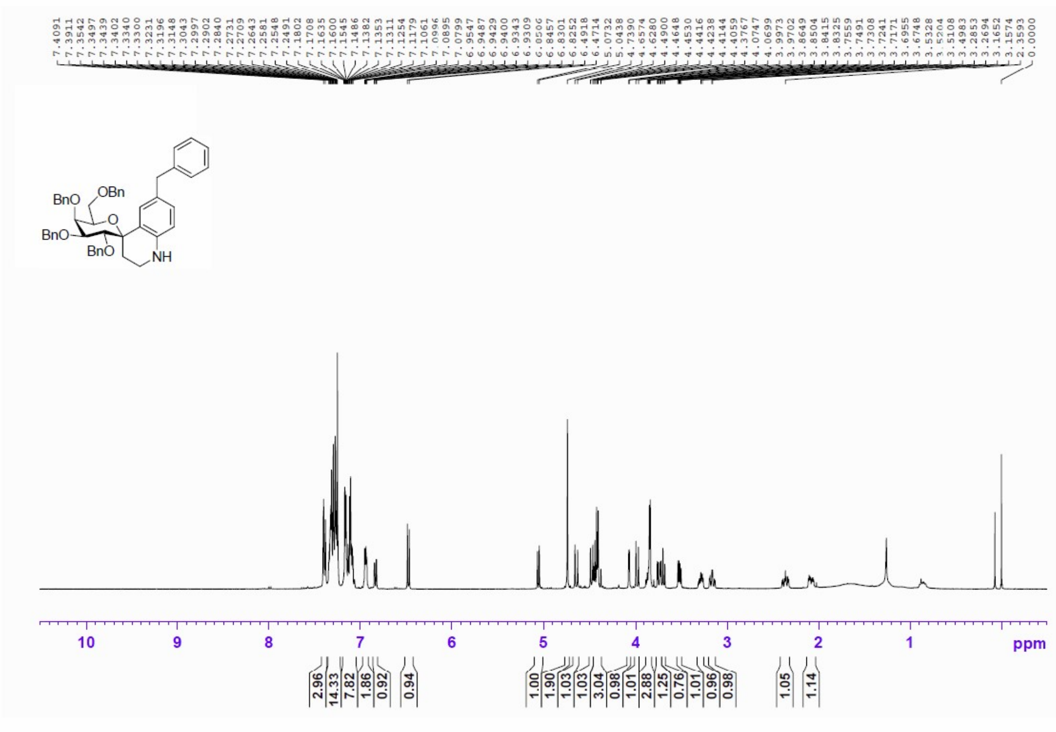
^{1}H NMR spectrum of **4q**



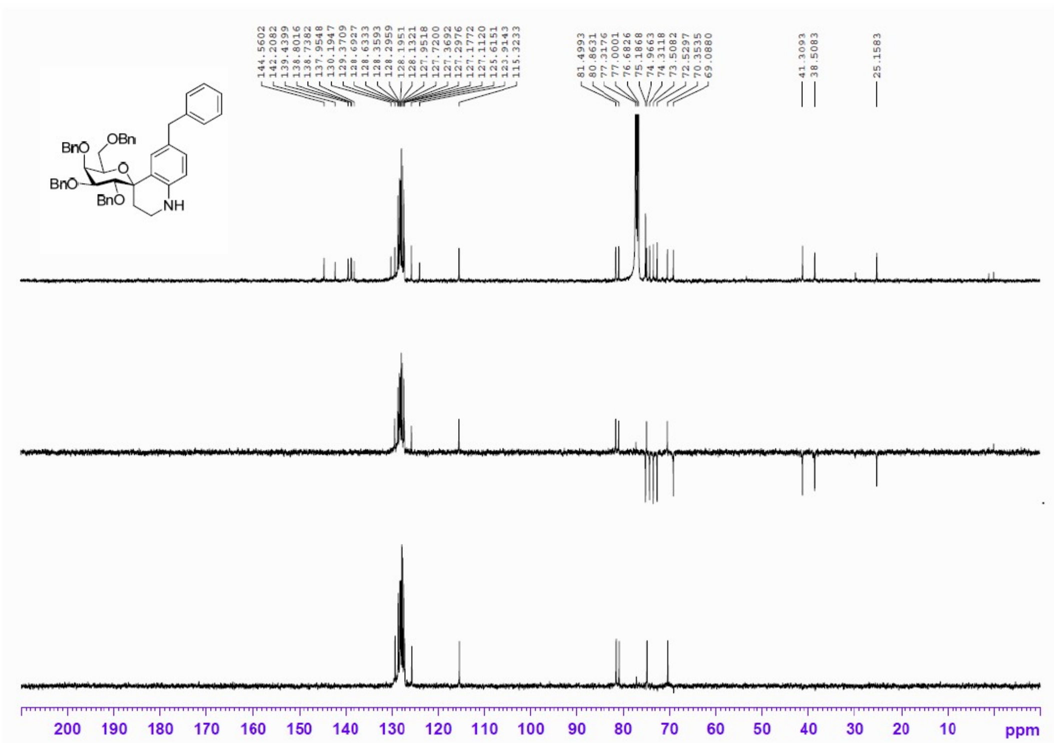
^{13}C NMR spectra of **4q**



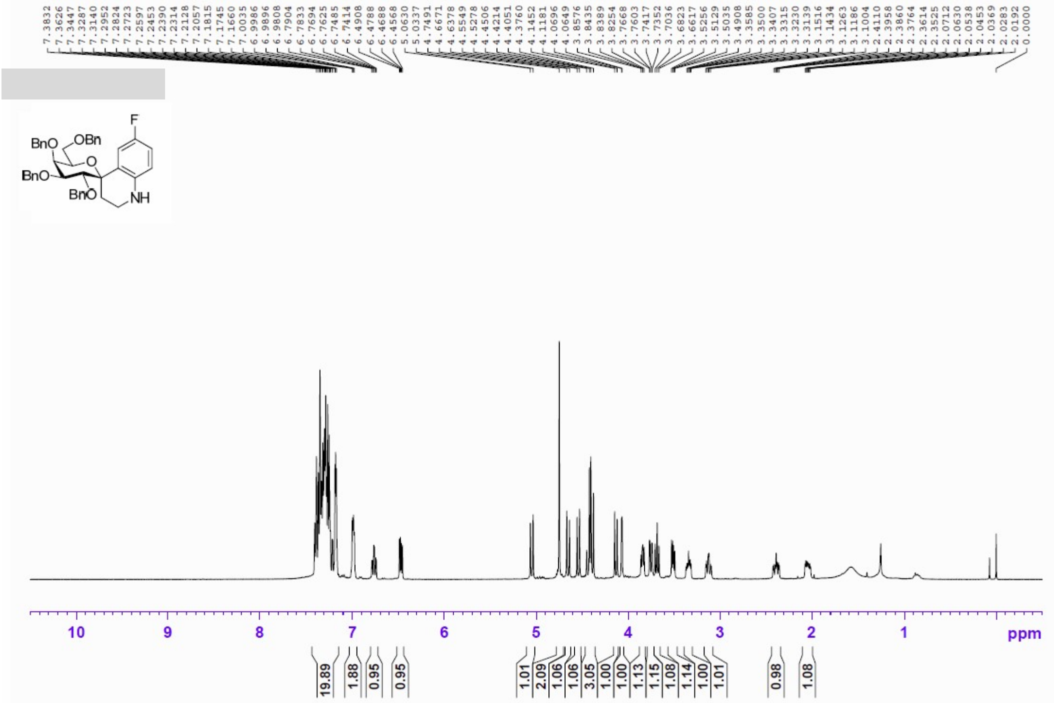
^{1}H NMR spectrum of **4r**



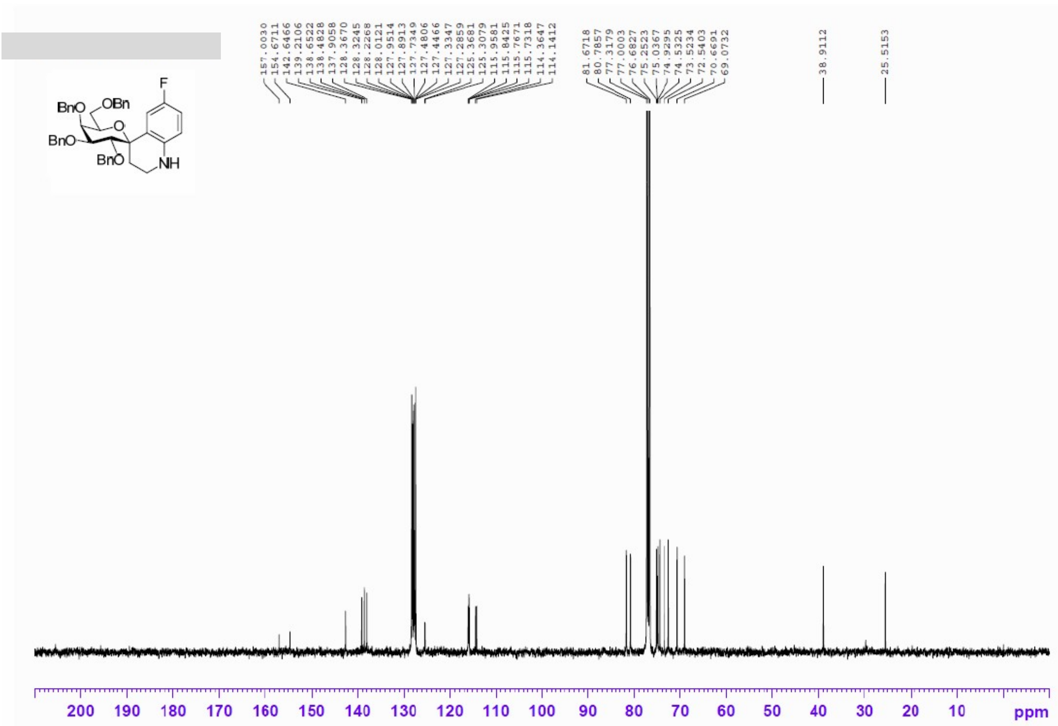
^{13}C NMR spectra of **4r**



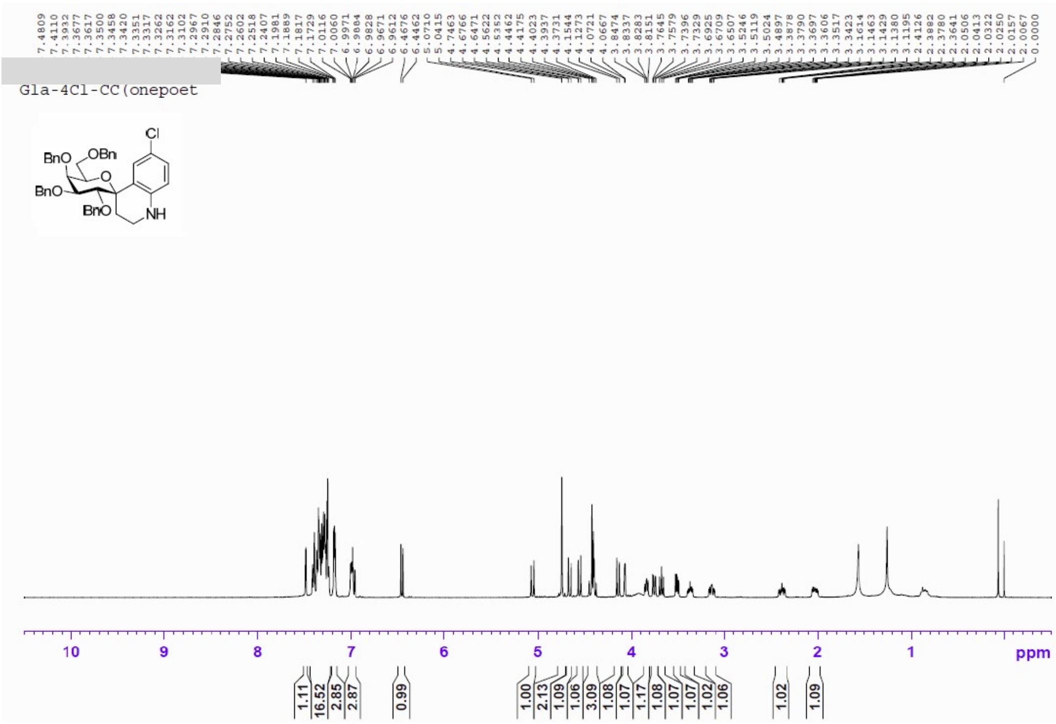
^{1}H NMR spectrum of **4s**



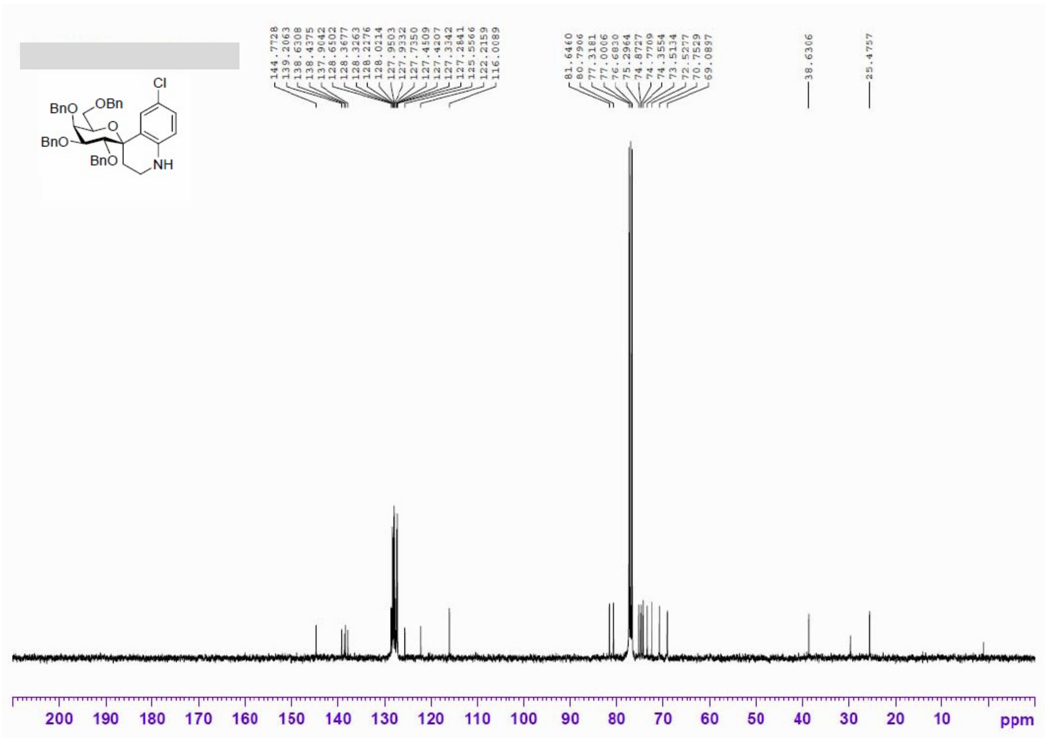
^{13}C NMR spectra of **4s**



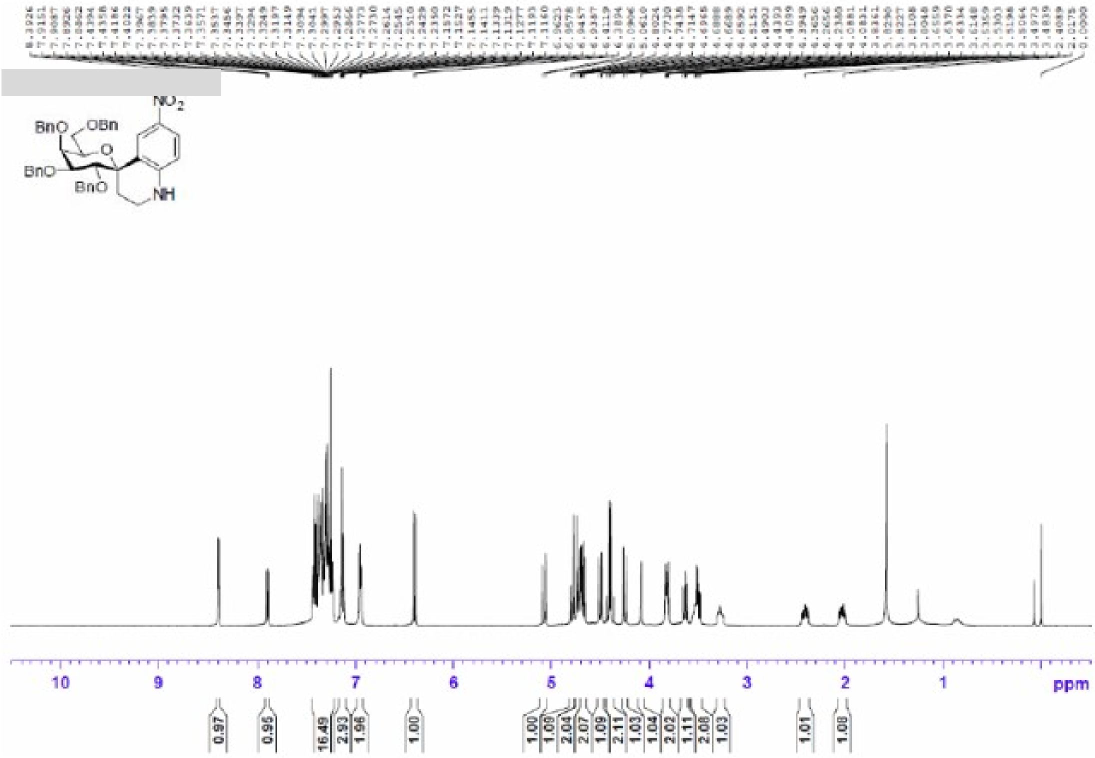
[1]H NMR spectrum of **4t**



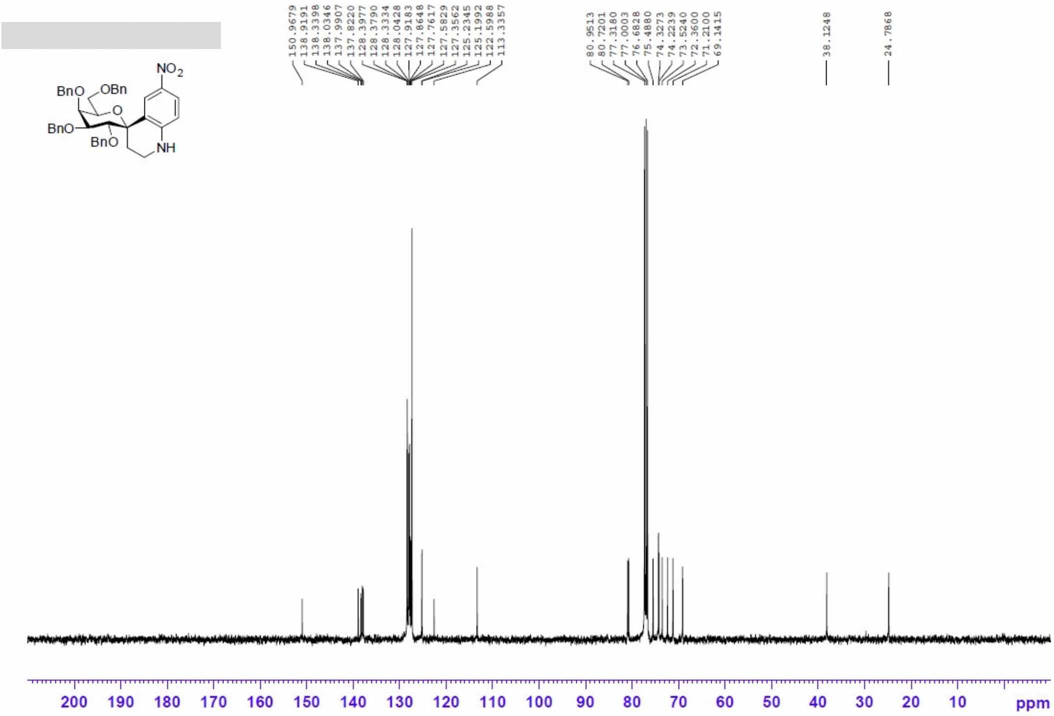
[13]C NMR spectra of **4t**



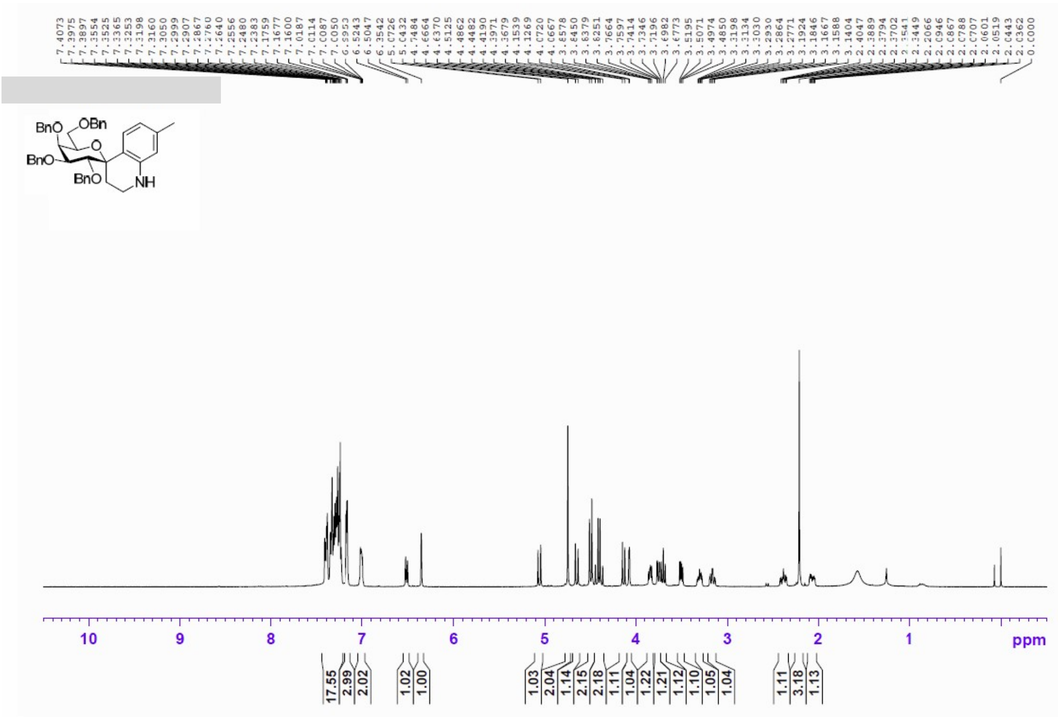
^{1}H NMR spectrum of **4u**



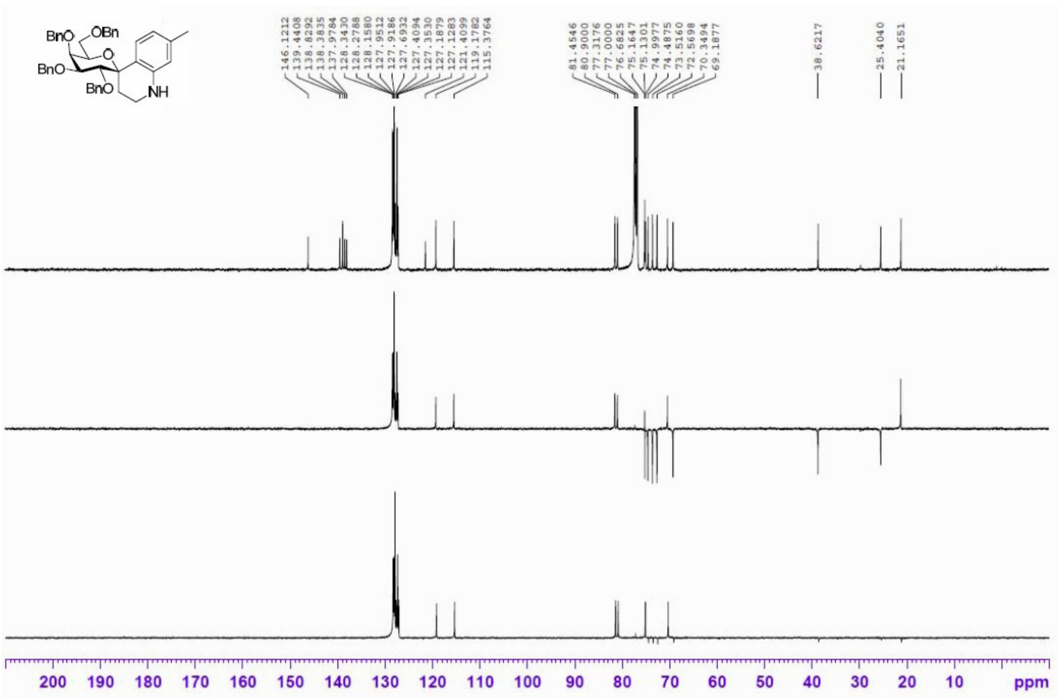
^{13}C NMR spectra of **4u**



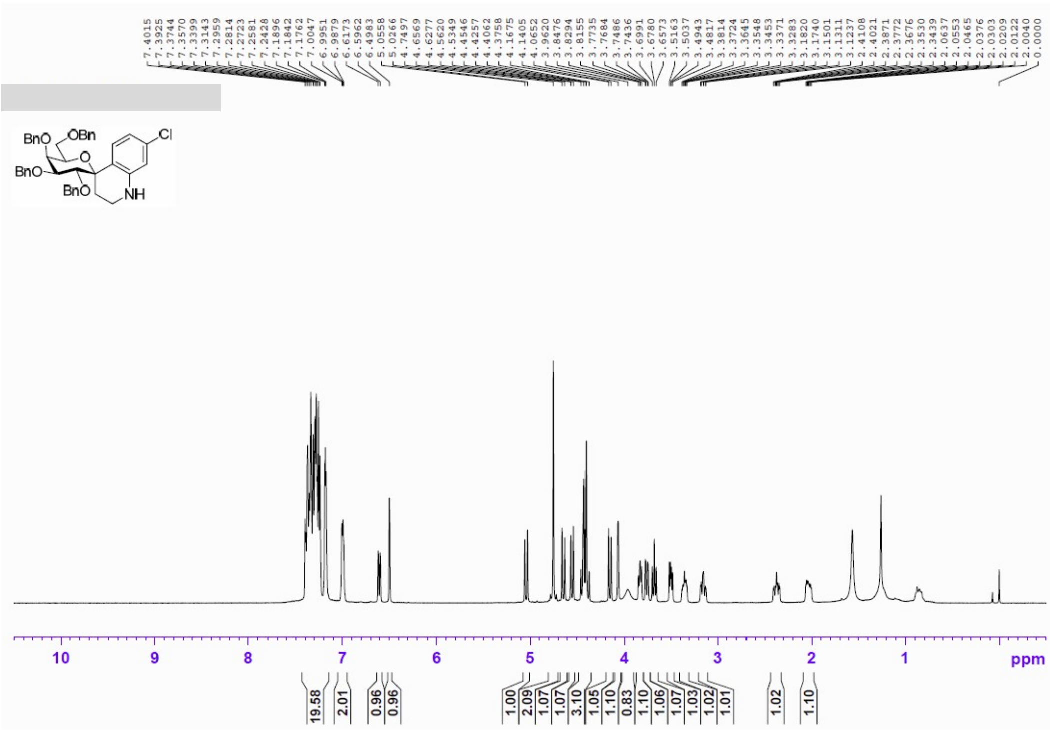
[1]H NMR spectrum of **4v**



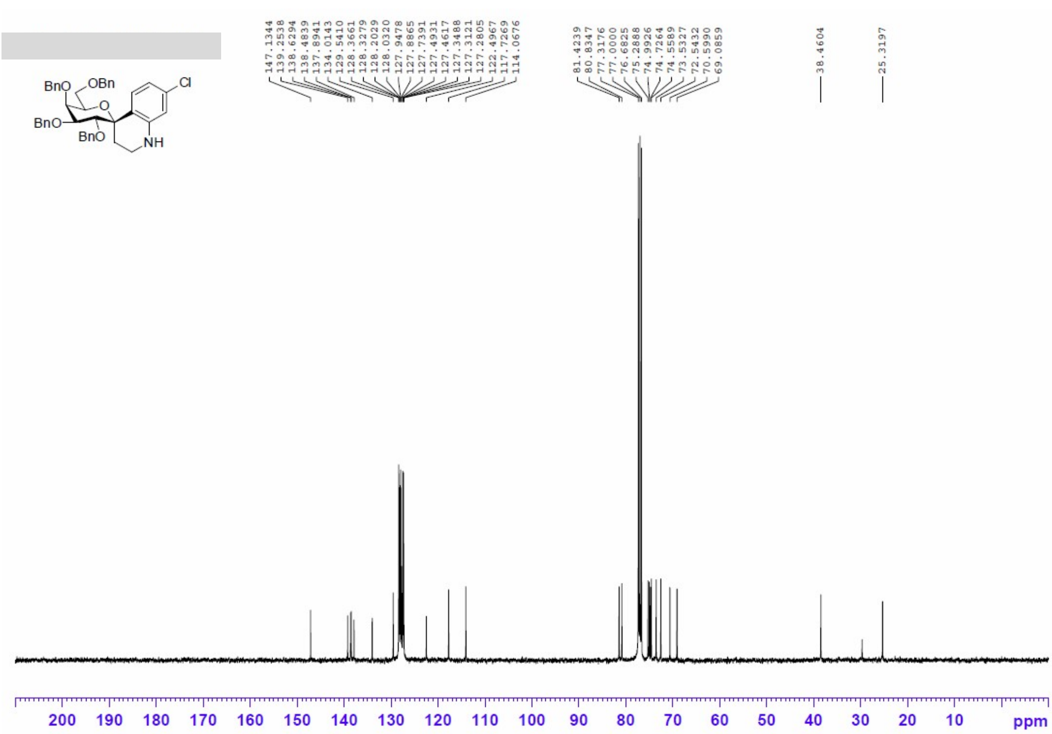
[13]C NMR spectra of **4v**



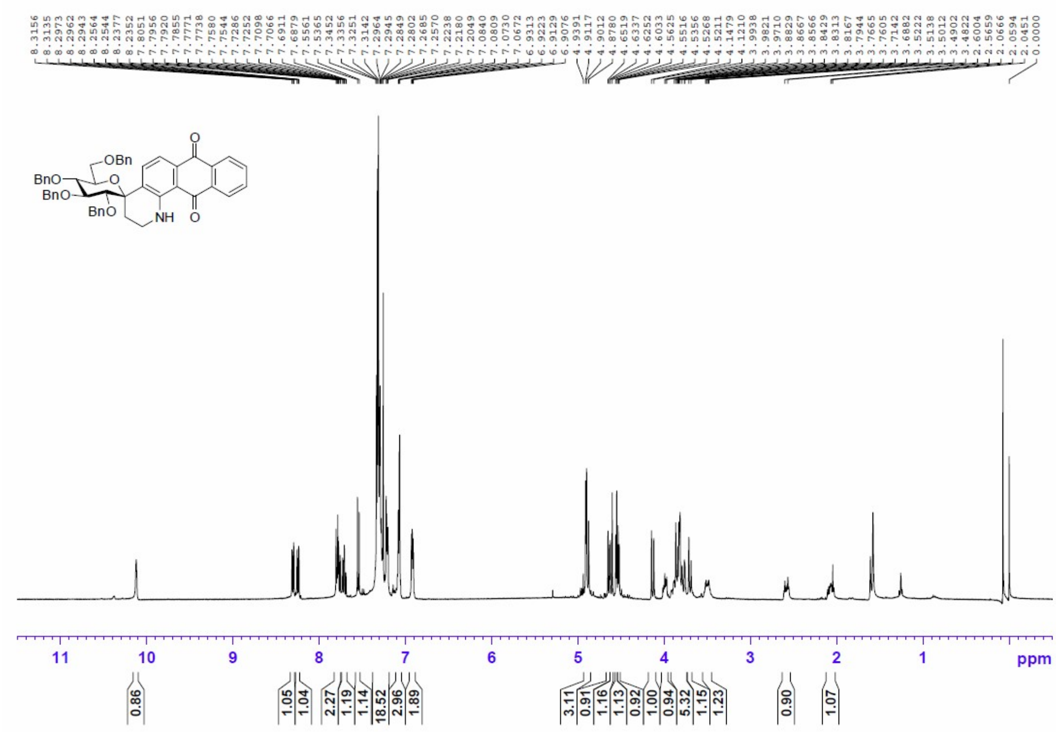
[1]H NMR spectrum of **4w**



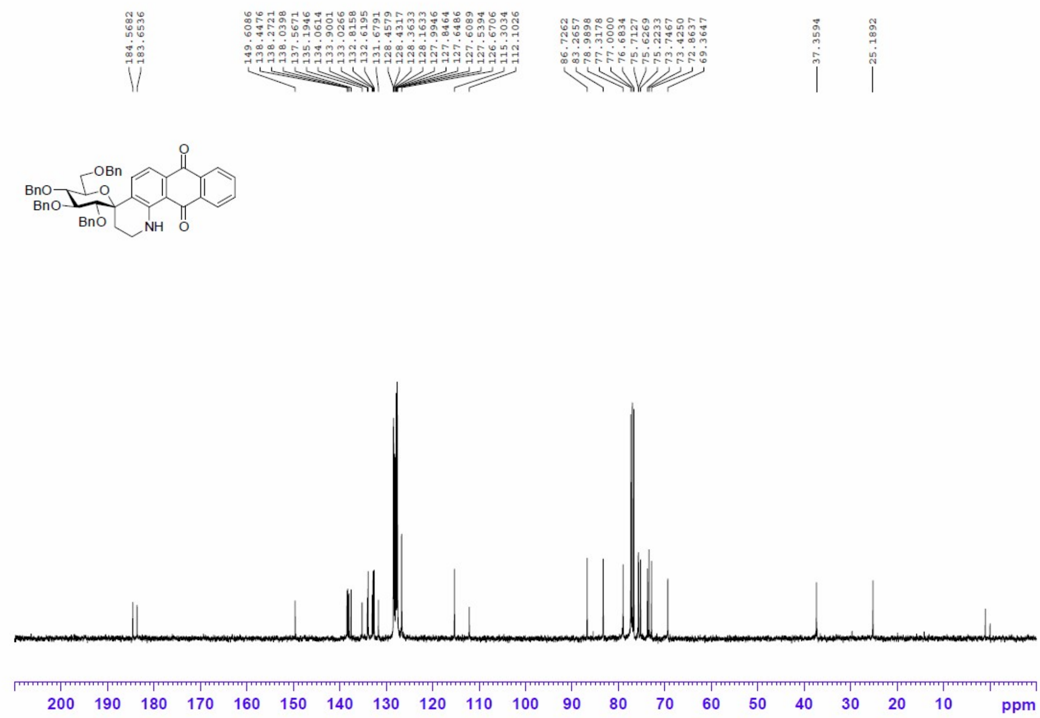
[13]C NMR spectra of **4w**



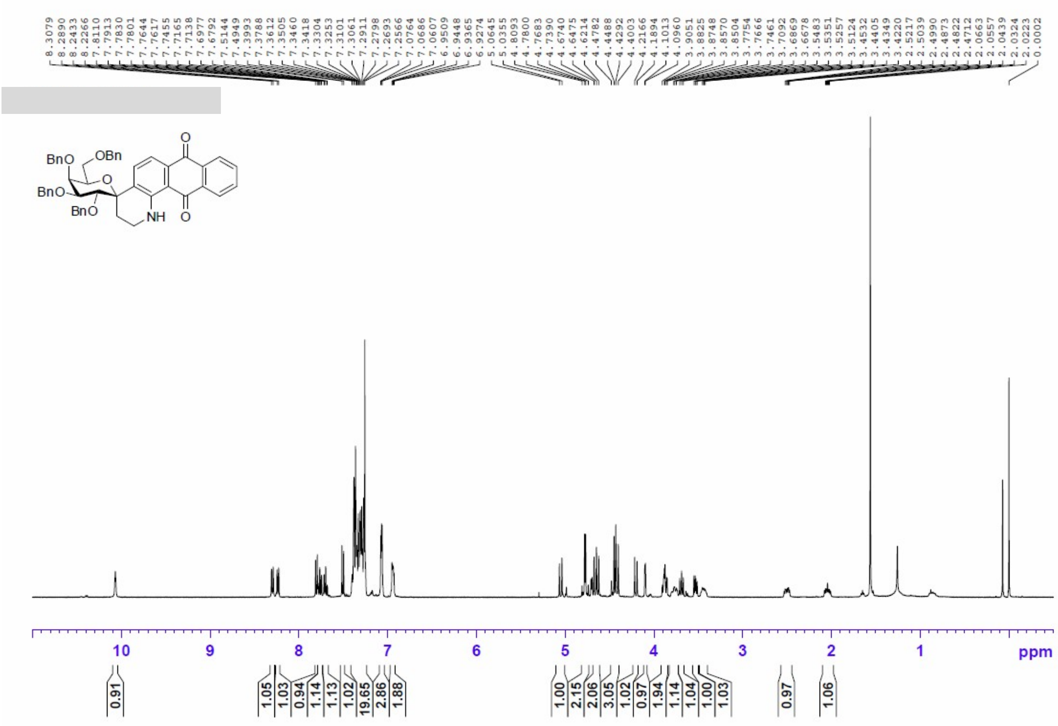
[1]H NMR spectrum of **4x**



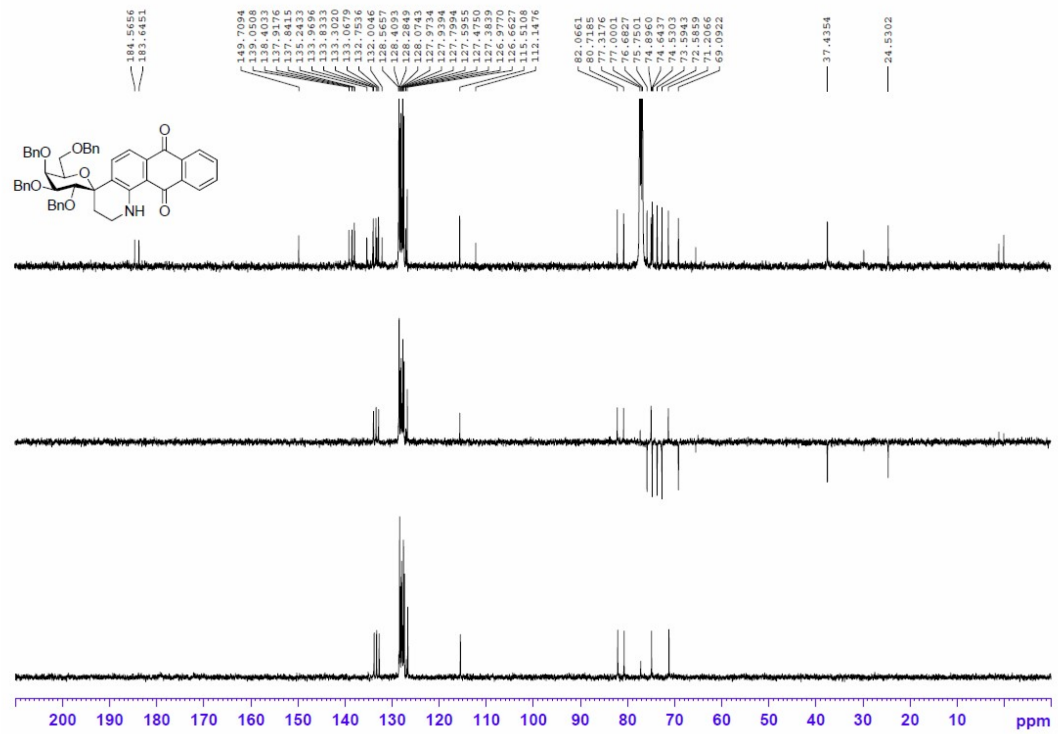
[13]C NMR spectra of **4x**



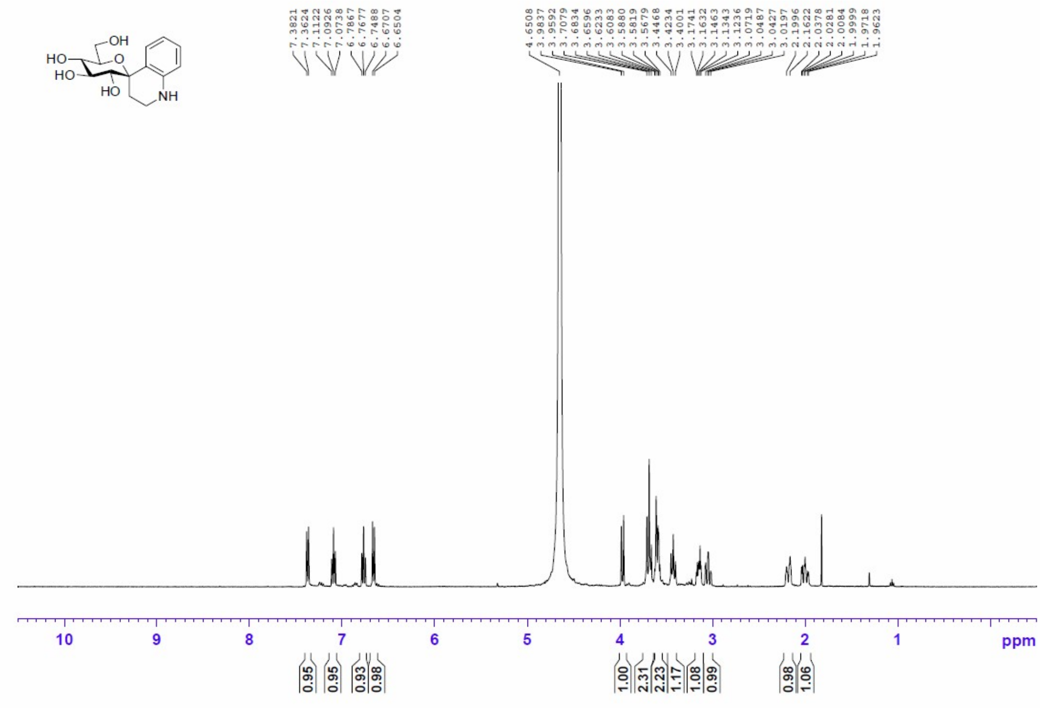
^{1}H NMR spectrum of **4y**



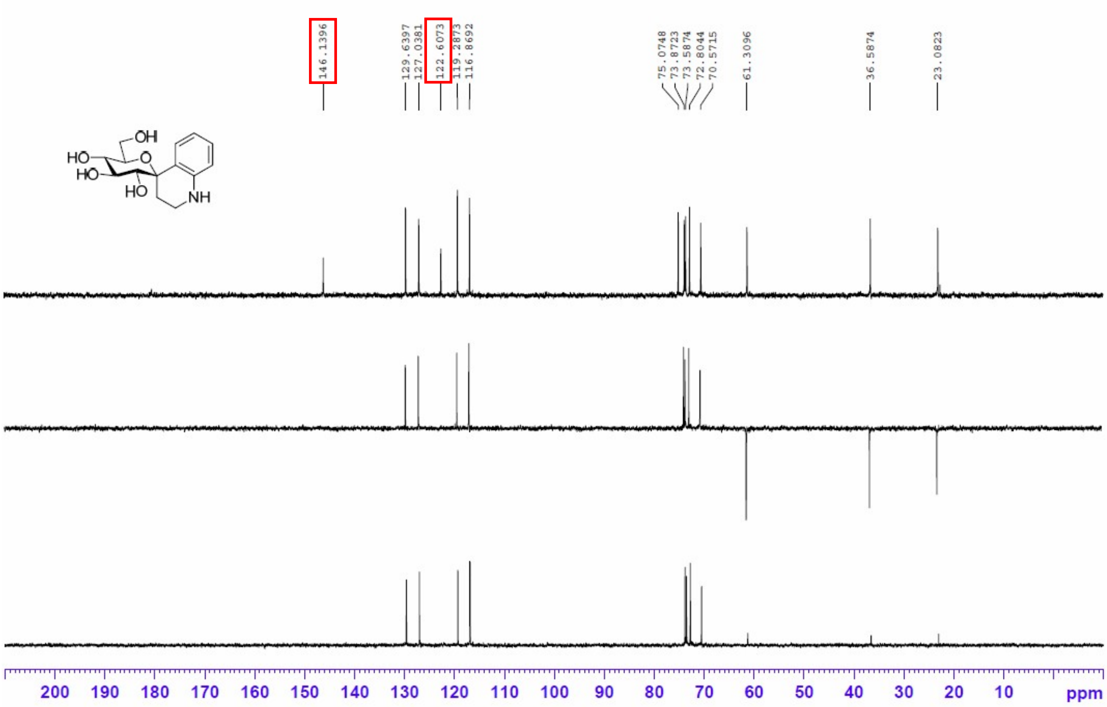
^{13}C NMR spectra of **4y**



^{1}H NMR spectrum of **5a**

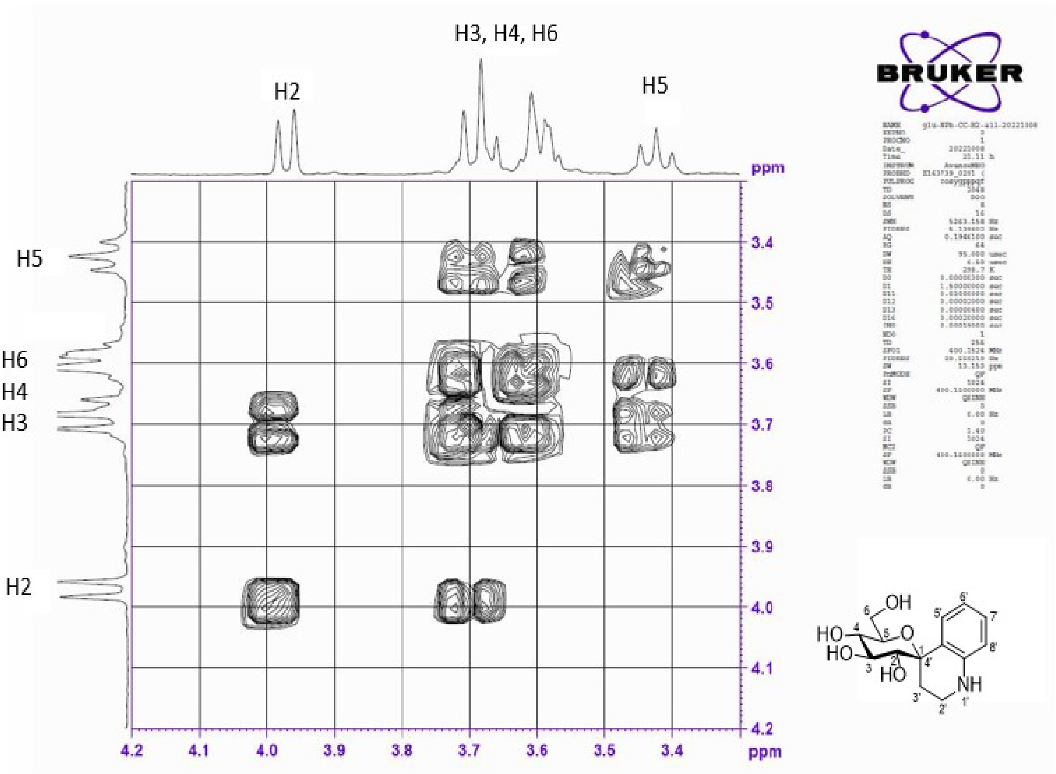


^{13}C NMR spectra of **5a**

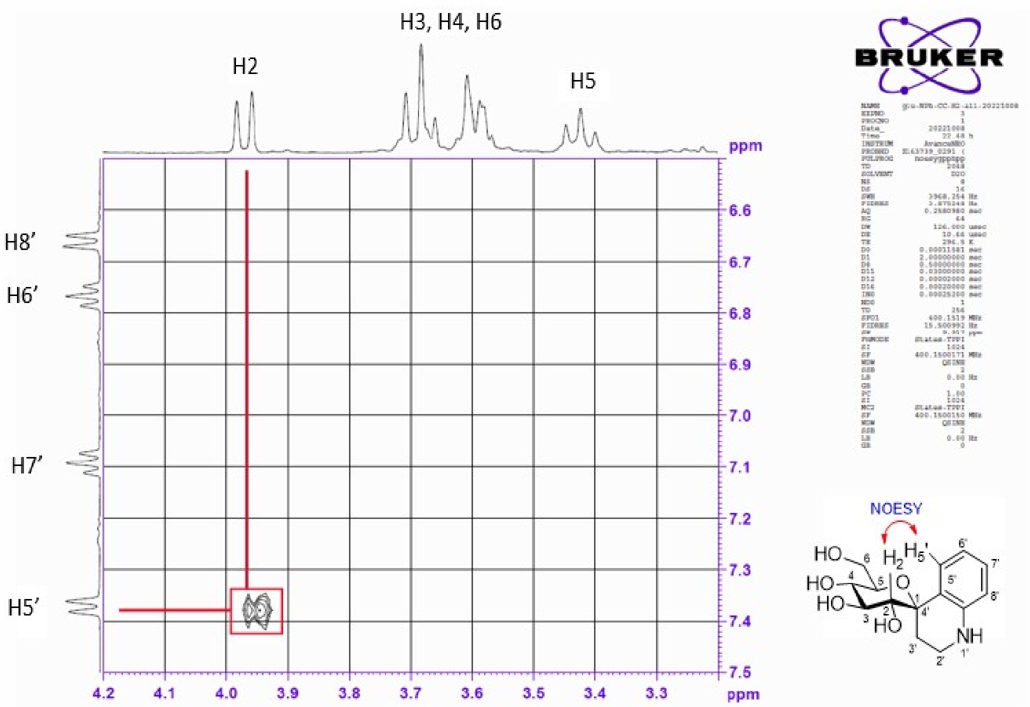


2D NMR spectra of 5a

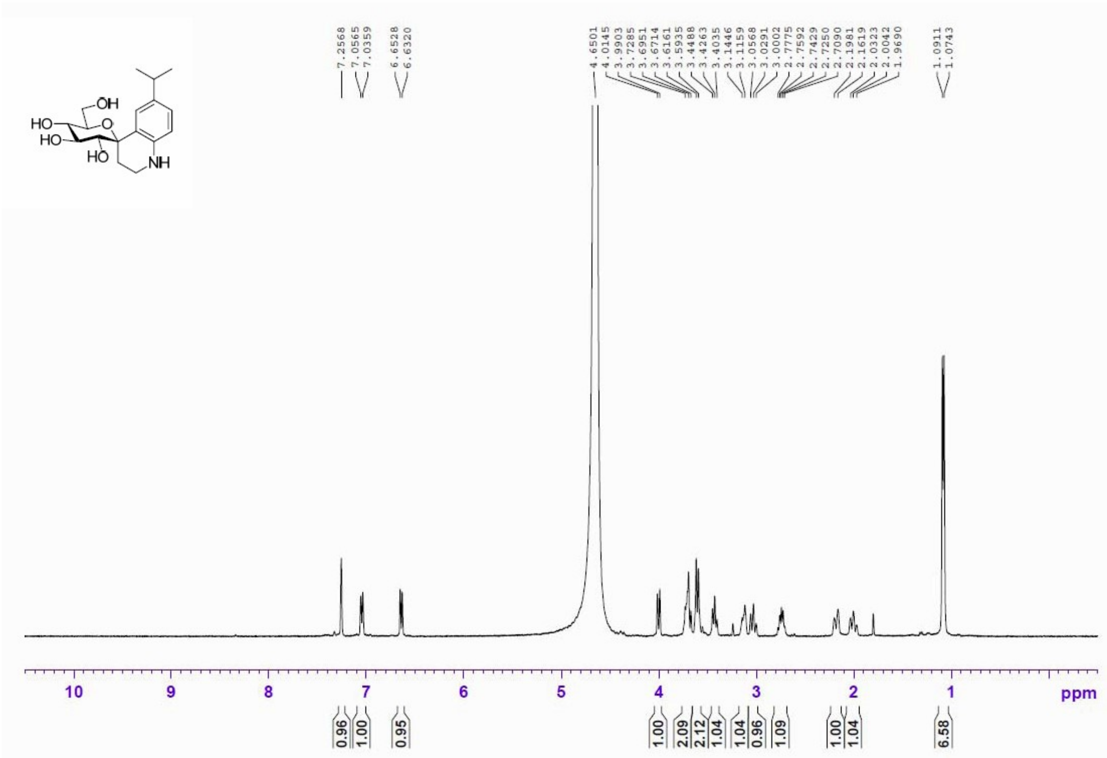
H-H COSY NMR spectrum of **5a**



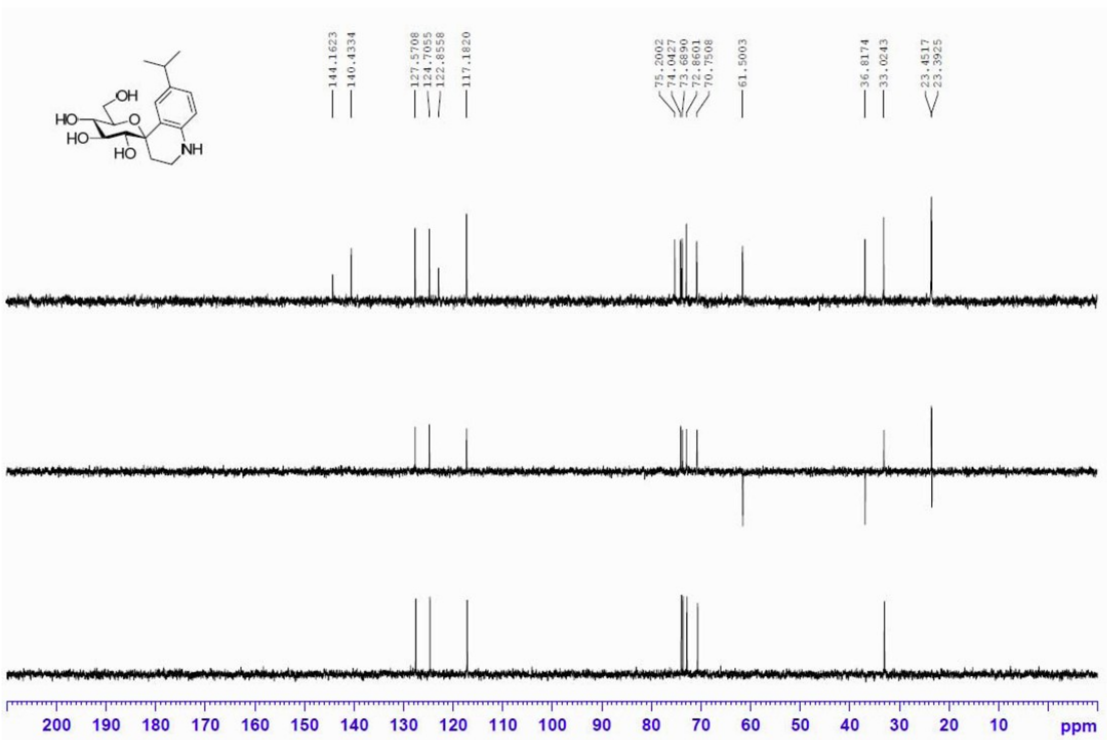
NOESY NMR spectrum of **5a**



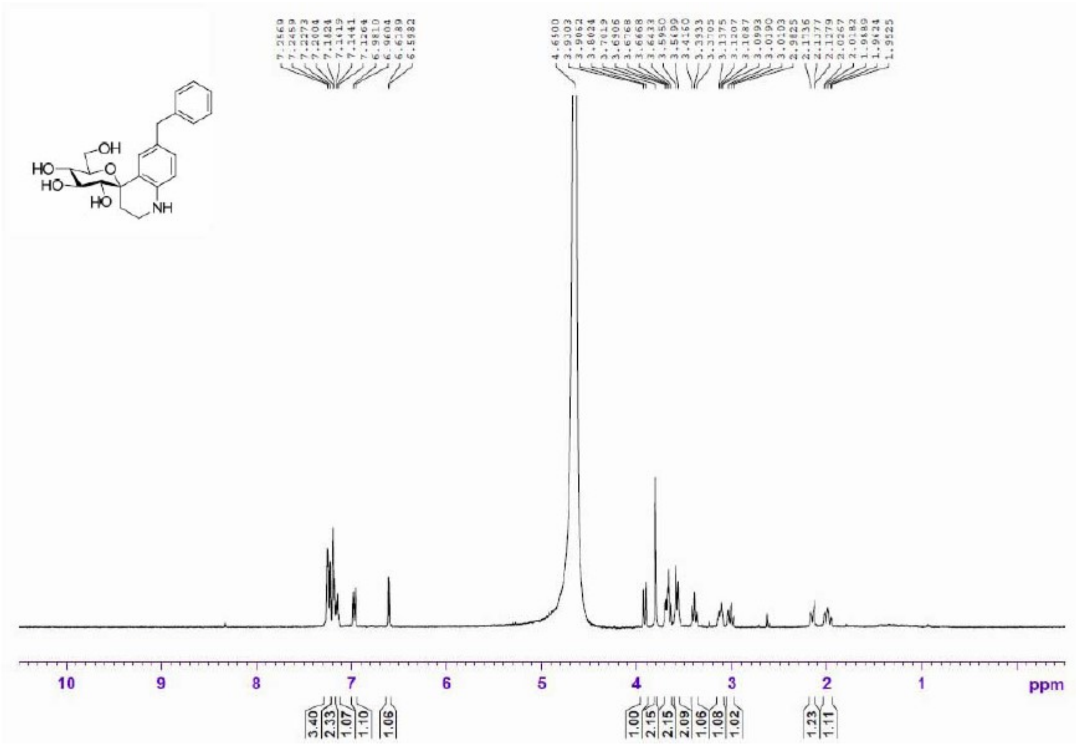
^{1}H NMR spectrum of **5b**



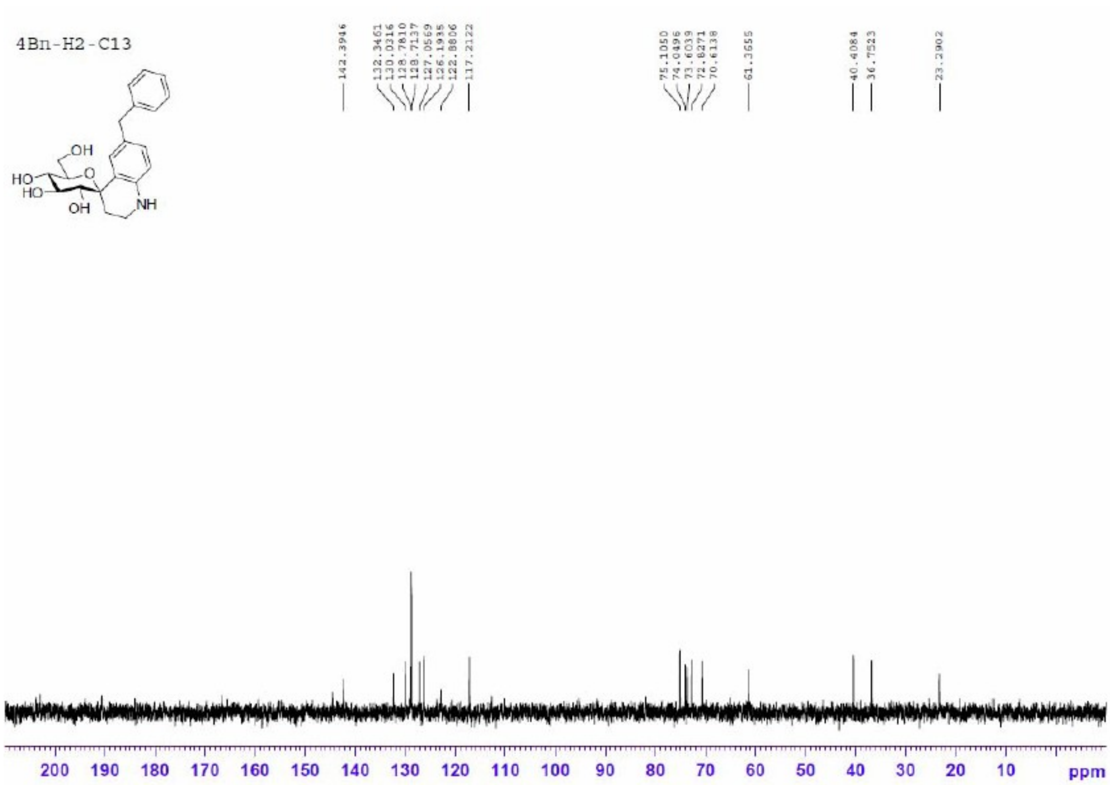
^{13}C NMR spectra of **5b**



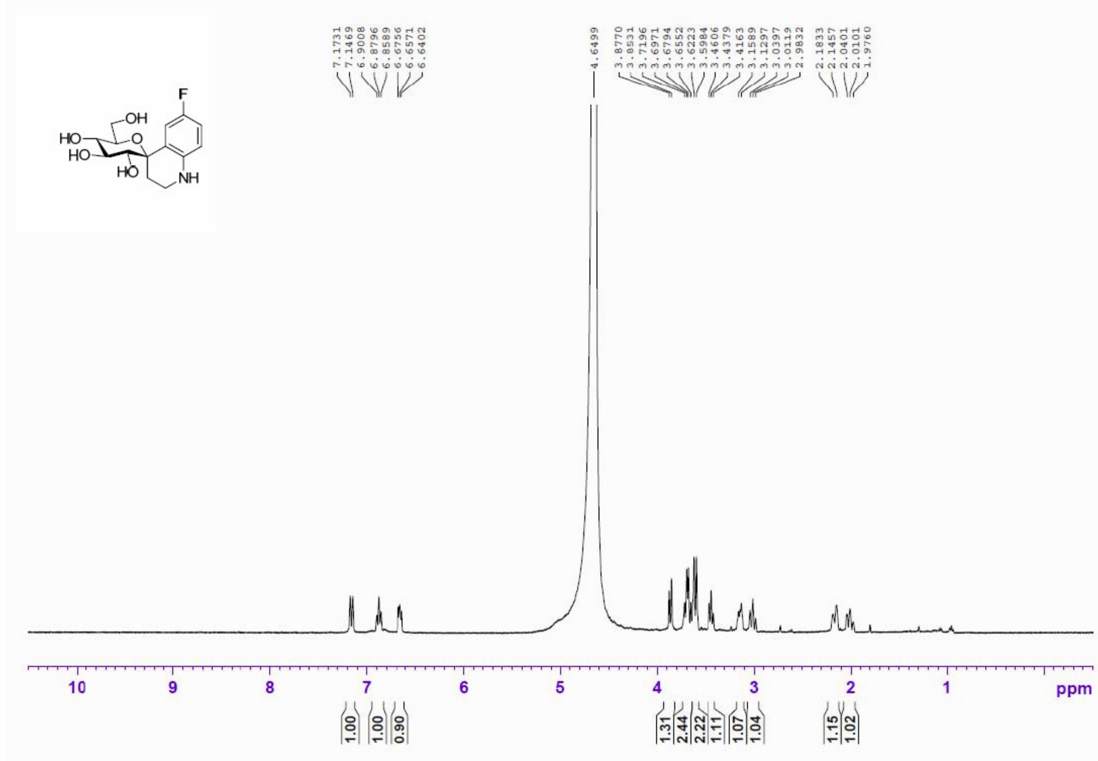
[1]H NMR spectrum of **5c**



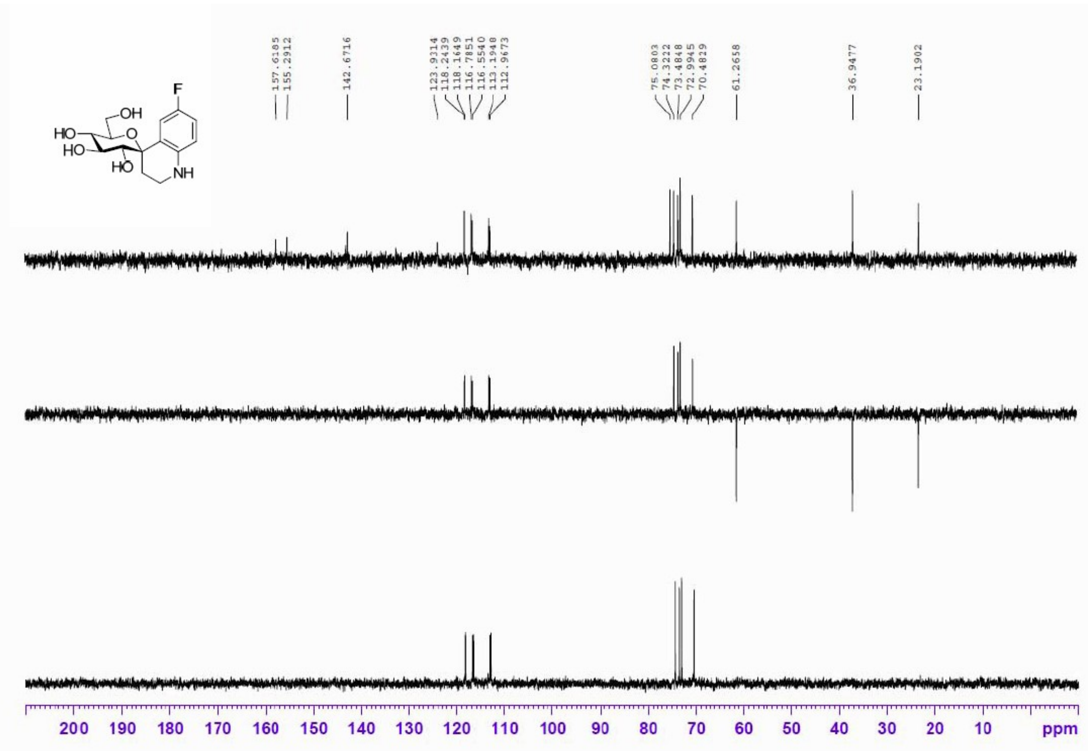
[13]C NMR spectra of **5c**



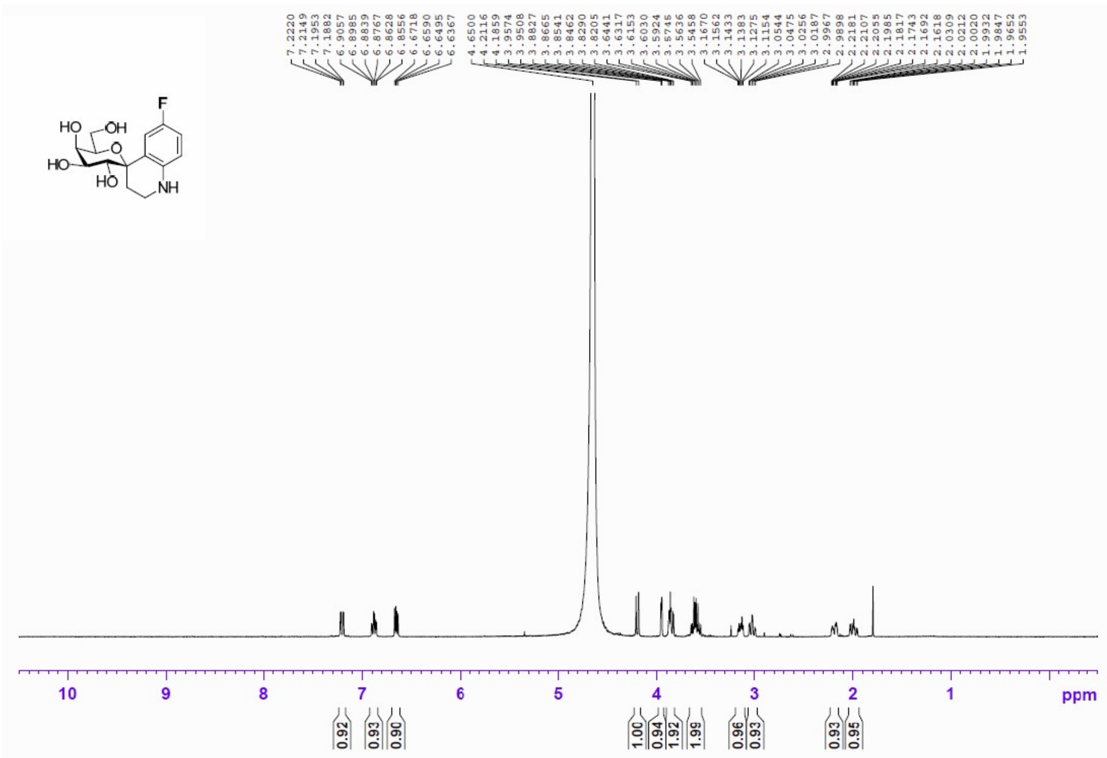
[1]H NMR spectrum of **5d**



[13]C NMR spectra of **5d**



[1]H NMR spectrum of **5e**



[13]C NMR spectra of **5e**